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## Process formulations and controlling factors of pesticide dissipation in artificial ponds: A critical review

Aya Bahi, Sabine Sauvage, Sylvain Payraudeau, Gwenael Imfeld, José-Miguel Sánchez-Pérez, Betty Chaumet, Julien Tournebize

### ► To cite this version:

Aya Bahi, Sabine Sauvage, Sylvain Payraudeau, Gwenael Imfeld, José-Miguel Sánchez-Pérez, et al.. Process formulations and controlling factors of pesticide dissipation in artificial ponds: A critical review. *Ecological Engineering*, 2023, 186, pp.106820. 10.1016/j.ecoleng.2022.106820 . hal-04062745

**HAL Id: hal-04062745**

**<https://hal.inrae.fr/hal-04062745>**

Submitted on 13 Nov 2023

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# 1 List of abbreviations

2

| <b>Abbreviation</b> | <b>Description</b>                                     |
|---------------------|--|
| TSS                 | Total suspended solids                                 |
| DP                  | Dissolved pesticides                                   |
| PP                  | Particulate pesticides                                 |
| OM                  | Organic matter   |
| OC                  | Organic carbon   |
| HRT                 | Hydraulic residential time                             |
| DOC                 | Dissolved organic carbon                               |
| POC                 | Particulate organic carbon                             |
| Re                  | Reynolds number  |
| vp                  | Vapor pressure   |
| FWS                 | Free water surface                                     |
| OECD                | Organization for Economic Co-operation and Development |
| PPDB                | Pesticide Properties                                   |
| NER                 | Non-extractable residue                                |
| SET                 | Settling   |
| RES                 | Resuspension   |
| VOL                 | Volatilization   |
| SOR                 | Sorption   |
| BIO                 | Biotransformation                                      |
| PHO                 | Photolysis   |
| HYD                 | Hydrolysis   |

3

# Process formulations and controlling factors of pesticide dissipation in artificial ponds: a critical review

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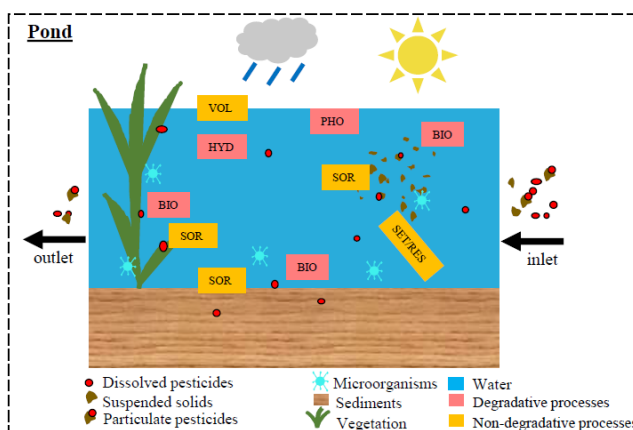
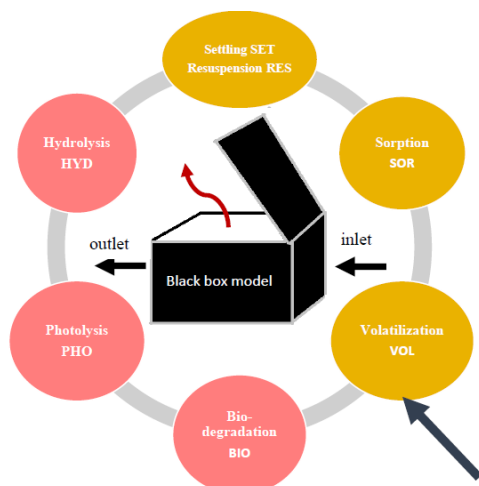
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## Graphical abstract:



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## 19 **Abstract**

20 Pesticides are a non-point source of pollution affecting the quality of drinking water supplies  
21 and aquatic environments. Many facilities are set up to reduce the transfer of pesticides from  
22 agricultural parcels into the environment, preventing their input into water bodies. Artificial  
23 ponds collecting runoff and erosion fluxes offer a complementary tool to mitigate pesticide  
24 transfer. Ponds are free-water surface-constructed wetlands, rarely dried out and not  
25 exceeding two meters in depth. Their main compartments include a water column, a sediment  
26 layer, living organisms, and suspended particles. The dissipation potential of ponds is due to a  
27 combination of physical, chemical, and biological processes that pesticides undergo in an  
28 interplay between different pond compartments. Although many studies on the dissipation  
29 potential of ponds focus on nitrates and suspended sediments, very little is known about the  
30 behavior of pesticides. Also, most studies evaluate a process individually without  
31 emphasizing its eventual interaction with other processes. Few papers address and compare  
32 mathematical formulations of pesticide transfer and transformation processes for artificial  
33 pond modeling. In this review, we investigate the interactions and contribution of multiple  
34 processes to artificial pond dissipation function by comparing their rates evaluated at different  
35 scales. We also discuss the mathematical formulations of processes and their relationship with  
36 pesticide properties. Our evaluation suggests that quantifying the contribution of each process  
37 to pesticide dissipation in artificial ponds is a major tool for hierarchizing dissipation  
38 processes. We believe that quantification and hierarchization may improve the overall  
39 artificial pond efficiency estimation. We anticipate this work to be the basis for developing a  
40 process-based model of pesticide fate in artificial ponds. The model will be particularly  
41 helpful in setting up the dimensioning criteria to design performant and efficient ponds to  
42 mitigate pesticide transfer into the environment.

### 43 **Keywords:**

44 Artificial pond; pesticide; dissipation; process; model, review.

45

**46 Highlights:**

- 47 • Identification and formalisms of dissipation processes of pesticides in artificial ponds
- 48
- 49 • Sorption as a key process for lowly soluble and hydrophobic pesticide dissipation
- 50
- 51 • Biotransformation enhanced in water-substrate interfaces favoring microbial activity
- 52
- 53 • Volatilization and hydrolysis can be mostly neglected
- 54
- 55 • Processes interplay contributes more significantly to the dissipation of pesticides
- 56
- 57 • Added value of descriptive process-based model of pesticide behavior in artificial
- 58 ponds
- 59
- 60
- 61
- 62
- 63

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94

## 95 **1. Introduction and definitions**

### 96 **1.1 Wetlands and artificial ponds**

97 In agriculture, various pests (e.g., weeds, insects, rodents, fungi, molds.) can significantly  
98 deteriorate the quantity and quality of agricultural products. In order to protect agricultural  
99 production, chemicals called "pesticides" are commonly used. Pesticides cover many  
100 compounds, including insecticides, fungicides, herbicides, rodenticides, molluscicides,  
101 nematicides, plant growth regulators, and others (Aktar et al., 2009). Due to their toxicity,  
102 pesticides represent a non-point source of pollution for the ecosystem and affect the quality of  
103 drinking water supplies and aquatic environments. Material solutions can be implemented as a  
104 complementary tool to safeguard water resources quality and mitigate pesticide input into  
105 water bodies, such as edge-of-field and riparian buffer strips, vegetated ditches, wetlands, and  
106 artificial ponds (Vymazal et al., 2015). In this paper, we will focus on constructed wetlands,  
107 especially artificial ponds, since they have the advantages of needing minimal operations, i.e.,  
108 being inexpensive to operate and construct and providing wildlife habitat (Sudarsan et al.,  
109 2021). A neat definition of wetlands and ponds and a description of their different types can  
110 be found in (Kadlec et al., 2008).

111 Artificial ponds are free water surface constructed wetlands, often kept wet and not exceeding  
112 2m depth (Z. Zhang et al., 2021), and they serve different purposes. Artificial ponds can be  
113 used as detention ponds to store water for irrigation purposes (Chaumet et al., 2022;  
114 Tournebize et al., 2015) or stormwater ponds to prevent flooding (Maillard et al., 2012).  
115 Artificial ponds are also used as complementary tools to treat contaminated agricultural water  
116 (Tournebize et al., 2017). These artificial ponds intercept agricultural water through runoff or  
117 subsurface drainage from cultivated agricultural plots. Artificial ponds are constructed upon  
118 an impermeable layer of sediments. The main artificial pond compartments are a water  
119 column, a sediment layer, living organisms (i.e., vegetation and microorganisms), and  
120 suspended particles. Since the late '80s, artificial ponds have been generally applied to treat  
121 various wastewaters, including agricultural water (Chouinard et al., 2014; Grinham et al.,  
122 2018; Wang et al., 2018; Zamora et al., 2019; Zhuang et al., 2019). It was widely reported that  
123 artificial ponds are able to reduce the transfer of chemicals (pesticides, organics, and  
124 inorganics pollutants), physical components (solid suspended particulates), and biological  
125 elements (bacteria) to natural water resources and preserve their quality (Kasak et al., 2018;  
126 Zheng et al., 2018). For example, artificial ponds had an important removal efficiency for  
127 organic matter, solids, and nitrogen up to 90% (de Oliveira et al., 2020; Tournebize et al.,  
128 2015). For pesticides, artificial pond efficiency can reach 97% for the organochlorine  
129 chemical group (Matamoros et al., 2006; Rose et al., 2006), 96% for the strobilurin/strobin  
130 group, and 84% for pyrethroids (Vymazal et al., 2015).

131 In that matter, significant research effort has been dedicated to understanding the fate of  
132 pesticides in artificial ponds and their link to the pond and pesticide properties (Bloomfield et  
133 al., 2006). In artificial ponds, pesticides are dissolved in water, attached to suspended  
134 particles, and sorbed on sediments and vegetation. The dissipation potential of artificial ponds  
135 results from a combination of transport, transfer, and transformation processes of pesticides.  
136 Transport processes carry pesticides following a water flow. Transfer processes allow the  
137 pesticide molecule to move from one phase to another (i.e., dissolved phase to particulate

138 phase or dissolved phase to gas phase), and transformation degrades and modifies the original  
139 chemical structure of pesticides.

140 Most studies could not distinguish the extent of removal processes because they depend on  
141 each other (Gregoire et al., 2009; Liu et al., 2019; Sahin et al., 2020) and thus could not model  
142 their impact on pesticide behavior. Additionally, previous reviews and studies (Stehle et al.,  
143 2011; Vymazal et al., 2015) focused on the efficiency of artificial ponds to remove pesticides  
144 and the ecological risk assessment of pesticides (Haith, 2010). However, they did not detail  
145 the processes behind pesticide dissipation, and they could not identify a direct link between  
146 ponds' efficiency and the pesticides' properties. Therefore, this paper investigates the  
147 relationship between dissipation processes and the main characteristics of pesticides in  
148 artificial ponds. Contrarily to the studies reviewed in this paper, this survey will evaluate  
149 plentiful pesticides with contrasting physicochemical properties and present the mathematical  
150 formulations of multiple processes evaluated from lab-scale to field-scale. These formulations  
151 are useful for modeling that help to estimate artificial pond efficiency and to optimize their  
152 implantation in agricultural areas.

## 153 **1.2 Processes governing the fate of pesticides in artificial ponds**

154 The dissipation of pesticides in artificial ponds results from the synergy between bio-  
155 physicochemical processes detailed thereafter. Several studies have proved the possibility of  
156 quantifying this dissipation and predicting the fate of pesticides by a black-box model  
157 (Braschi et al., 2022). However, a black box approach does not explicit the origin of pesticide  
158 dissipation and does not detail the contribution of each process since it only considers a single  
159 dissipation rate  $k_{\text{diss}}$  ( $\text{d}^{-1}$ ) (Yuan et al., 2020).

160 In this review, we will describe and present different estimation methods of processes behind  
161 pesticide dissipation in artificial ponds. The form under which pesticides are introduced to the  
162 artificial pond depends on how agricultural water is drained into the artificial pond. If the  
163 watershed is drained with significant subsurface flow, pesticides are more likely to be  
164 dissolved rather than particulate (Braschi et al., 2022; Le Cor et al., 2021). In contrast,  
165 pesticides can be present in dissolved and particulate phases if runoff occurs. Gramlich et al.  
166 (2018) assumed that subsurface drainage reduces erosion risk, while runoff may increase it.  
167 Dissolved Pesticides (DP) in water bodies are widely studied in the literature, whereas few  
168 studies focus on Particulate Pesticides (PP) (Climent et al., 2019). PP are transported within  
169 the artificial pond along with TSS following the water flow. According to the hydraulic  
170 regime of the artificial pond, PP can settle on the sediment bed or be suspended back to the  
171 water. In contrast, DP can be bound to the solid surfaces available in the artificial pond  
172 through sorption. Sorbed DP can be released back into water through desorption. DP can also  
173 be transported to the atmosphere when volatilized or uptakes by the plants growing in the  
174 artificial pond. On the other hand, pesticides can be a subject of transformation processes,  
175 whose prevailing drivers are microorganisms, solar radiation, and hydrolysis.

176 Processes involved in pesticides dissipation in artificial ponds depend on many factors such as  
177 the characteristics of the soil (i.e., Organic matter (OM), organic carbon (OC), and clay  
178 content), water physicochemical properties (pH, temperature (T) and redox conditions),  
179 vegetation, and the hydraulic conditions of the artificial pond (Papaevangelou et al., 2017;  
180 Vymazal et al., 2015). The mitigation of pesticides in artificial ponds also depends on the  
181 pesticide's physicochemical properties. The main physicochemical properties of a pesticide  
182 include mobility, hydrophobicity, the solubility in water (S), and the pesticide half-life ( $DT_{50}$ )



183 - the time required for the dissipation of 50% of the concerned substance (Gregoire et al.,  
184 2009).

185 The properties of pesticides and the processes behind their dissipation in artificial ponds will  
186 be detailed afterward.

### 187 **1.3 Hydraulics of artificial ponds**

188 The hydraulic performance is a key factor controlling the pesticide dissipation function of a  
189 artificial pond. The hydraulic performance of artificial ponds includes lowering peak flow and  
190 limiting sediment export from agricultural parcels to natural water bodies (Passeport et al.,  
191 2010; Tournebize et al., 2013). Artificial ponds hydraulic parameters include (i) The hydro  
192 period (Bojcevska et al., 2007; Convertino et al., 2013; Liu et al., 2019; Prochaska et al.,  
193 2007) and (ii) The hydraulic residence time (HRT) of the water within the artificial pond (J.  
194 Holland et al., 2004; Kjellin et al., 2007).

195 The hydraulic performance of artificial ponds depends on design parameters such as depth,  
196 the layout of the inlet and outlet, and plant spacing. In this subsection, we will describe the  
197 impact of design parameters on the hydraulic performance of artificial ponds.

198 Multi tracer experiments showed that shallow water depth was an essential factor enhancing  
199 sorption and that pesticide load reduction was more significant in shallow artificial ponds than  
200 in deep ones (Lange et al., 2011). A low water depth allows a uniform fluid distribution  
201 compared to higher depths. The uniformity of the fluid flow decreases the hydraulic dead  
202 zones and increases the effective volume, which is the artificial pond volume used for  
203 pesticides dissipation (Rayen et al., 2019).

204 Globally, an artificial pond volume can be divided into three hydraulic zones (C. J. Martinez  
205 et al., 2003; Werner et al., 2000):

- 206 1. The main channel with the preferential flow.
- 207 2. The mixing zone is a temporary storage zone showing exchanges with the main  
208 channel.
- 209 3. The dead zone is more isolated from the main channel than the mixing zone.

210 Tracing studies showed that water is transported mainly by convection in the main channel,  
211 while it is transported by dispersion in the isolated zones (mixed and dead zones). The HRT in  
212 isolated zones is longer than in the main channel. Thus, isolated zones could enhance  
213 dissipation processes such as sorption, settling, and degradation (Gaulhier et al., 2018). The  
214 main channel is where short circuits in the water flow can occur, causing the transport of  
215 water from the inlet to the outlet by preferential flow, which decreases the HRT and effective  
216 volume of the pond (Vieira et al., 2018). Another controlling parameter of the artificial pond  
217 hydraulic performance is the inlet/outlet design. Shilton et al. (2003) reported that positioning  
218 the outlet in an isolated zone from the main channel avoids short-circuiting issues and  
219 maintains the maximum hydraulic performance of artificial ponds. In addition, vegetation  
220 density slows down water velocity and increases the HRT (Gu et al., 2017). Increasing the  
221 hydraulic residence time (HRT) increases the contact time between pesticides and pond  
222 substrates, giving pesticides more time to be sorbed, settled, or degraded.

223 A good hydraulic performance also guarantees an optimistic interception of agricultural water  
224 by catching the highest concentrations of pesticides (during the post-application period) in  
225 minimum water volumes through off/on stream artificial ponds (Passeport et al., 2013;  
226 Passeport et al., 2010).

227

228 Usually, the risk of transfer of a pesticide is evaluated by the FOCUS models to decide  
229 whether to be authorized for use or not. However, since pesticides are still transferred to the  
230 environment after their application and their concentration in water resources than the RAC  
231 (regulatory acceptable concentrations) (Gassmann et al., 2015; Halbach et al., 2021; Tang et  
232 al., 2012), this theoretical study can be improved. Therefore, this work is based on a detailed  
233 bibliographic analysis to present the required knowledge to understand the behavior of  
234 pesticides after being applied on agricultural plots and intercepted by artificial ponds. This  
235 knowledge is useful for developing a simple and robust conceptual model to simulate the fate  
236 of pesticides in artificial ponds and then at the catchment scale, like the models developed for  
237 nutrients (Hantush et al., 2013; Kalin et al., 2017; Walker Jr et al., 2011). Modeling can also  
238 improve the understanding and hierarchization of the dissipation process and optimize its  
239 implantation in agricultural areas. Therefore, the next section will describe the key processes  
240 behind pesticide dissipation in artificial ponds and their mathematical formulations used in  
241 modeling.

## 242 **2. Description and modeling of dissipation processes in artificial ponds**

243 Modeling is an efficient, comprehensive tool for assessing and setting up facilities to treat  
244 contaminated environments (Warren et al., 2002). There are mainly two types of models that  
245 describe pesticide fate in the environment, (i) Physical 3D and 2D models that simulate the  
246 hydraulic performance of wetlands by considering water velocity profiles and the vegetation  
247 impact of the flow (Carleton et al., 2010; Luo et al., 2016; Christopher J. Martinez et al.,  
248 2003; Tsavdaris et al., 2013). (ii) Conceptual models that simulate the biogeochemistry and  
249 the dissipation performance of the wetland for a large-scale application (Gobas et al., 2018;  
250 Willkommen et al., 2018). The asset of this paragraph is to identify and describe processes  
251 behind pesticide dissipation in artificial ponds, along with their mathematical formulations  
252 established as part of conceptual models.

253 Our literature investigation showed that researchers had widely discussed the fate of  
254 pesticides in artificial ponds. Although, most studies are generally limited to one pesticide or  
255 one specific process evaluation and are rarely supported by mathematical formulae. However,  
256 we assume that mathematical formulations allow the integration of processes into a  
257 computational model to quantify and predict the fate of contaminants in artificial ponds. The  
258 originality of this review lies in the description of the main processes influencing the behavior  
259 of multiple pesticides in artificial ponds, namely transport, sorption, and transformation  
260 processes. The evaluation and formulation of these processes are necessary to develop  
261 predictive models for pesticides dissipation in artificial ponds (Papaevangelou et al., 2017;  
262 Saaristo et al., 2018). In this section, we will investigate the behavior of multiple pesticides  
263 with contrasting physicochemical proprieties and describe different methods currently  
264 employed to evaluate and formulate the processes controlling dissipation in artificial ponds.

### 265 **2.1 Transport of pesticides**

266 Pesticides reaching artificial ponds can be dissolved in water or associated with dissolved  
267 organic carbon (DOC). They can also be bound to the organic fraction of suspended matter  
268 (i.e., particulate organic carbon (POC)), featuring pesticides in a particulate form. PP are  
269 carried along with suspended matter throughout the pond artificial pond due to water  
270 movements. PP can be deposited on the sediment bed due to settling and released back to  
271 water through resuspension. Settling and resuspension are transport processes that strongly  
272 depend on the particle size and the strength of the water flow in pond artificial ponds.

273 Pesticides can also be the subject of advection, dispersion, and diffusion processes within the  
274 water column and pore water of the sediment layer. According to the Hjulstrom curve, the  
275 water velocity in the artificial pond can determine which transport process is prevailing  
276 (Hjulstrom, 1935).

### 277 2.1.1 Settling

278 Settling is a physical transport process through which suspended particles in water settle on  
279 the sediment bed of artificial ponds. Settling depends on the particle size of pesticides, water  
280 velocity and turbulence, temperature, and water column depth (Kadlec et al., 2008).

281 Settling has been efficient in the water-quality improvement function of artificial ponds,  
282 especially in lower flows, since suspended particles, on which pesticides may be attached, can  
283 leave the water column while settling on the sediment bed (O'Geen et al., 2010). Settling is  
284 enhanced when vegetation covers a significant surface of the artificial pond; emergent  
285 macrophytes slow down water flow and amplify settling (Vymazal, 2013). In addition, stems  
286 and leaves in the water column obstruct water flow and dissipate the energy required to  
287 support particle suspension (Schmid et al., 2005). Rose et al. (2008) pond ( $0.021 \text{ h}^{-1}$ ). A small  
288 water depth was also reported that the settling rate in a vegetated artificial pond ( $0.042 \text{ h}^{-1}$ )  
289 was double the rate estimated in a non-vegetated artificial to promote the settling process; it  
290 fosters plant growth and shortens the settling distance for particles (Lange et al., 2011). It is  
291 valid for water depths between 20 cm and 50 cm (Braskerud, 2002). Pesticides associated  
292 with fine suspended particles may hardly be retained in ponds since fine particles (clay and  
293 silts) are highly transported across preferential pathways where the HRT is low (see section  
294 1.3) (Maynard, 2009). The settling of PP is more likely to occur in hydraulically isolated  
295 zones with lower water flow and higher HRT (Gaulhier et al., 2020; Passeport et al., 2010).  
296 Ponds with the highest settling rate are the ones receiving agricultural surface runoff (Fiener  
297 et al., 2003; Zhang et al., 2011), where the intercepted agricultural water is heavily loaded  
298 with coarser ( $>200 \mu\text{m}$ ) particles from the fields (Li et al., 2017). It is due to the higher TSS  
299 load from erosion that is less available in artificial ponds collecting subsurface drainage water  
300 (Koskiaho, 2003; Maillard et al., 2011). It was also suggested that coarse particles settle  
301 before the water is distributed across pond compartments, unlike fine particles requiring a  
302 longer time to settle. As a result, fine particles become more concentrated downstream of the  
303 pond (Gan et al., 2005) because gravity induces the settling of heavy particles ( $>36 \mu\text{m}$ ) (i.e.,  
304 sand) more than lighter particles ( $<2 \mu\text{m}$ ) (i.e., clay and OM) (Fiener et al., 2003). Several  
305 studies suggested that a large proportion of highly hydrophobic organic substances in artificial  
306 ponds were retained by settling pesticide-laden solids (sorbed on suspended solids) (Luo et  
307 al., 2009; Matamoros et al., 2006; Rose et al., 2008). Therefore, settling may not be sufficient  
308 to trap pesticides with a stronger affinity to fine suspended particles in ponds. Consequently, a  
309 higher HRT and vegetation are required to increase the settling of fine PP (Budd et al., 2009,  
310 2011; Fiener et al., 2003).

311 Settling was commonly integrated with an accumulation rate expressed empirically in  
312 pesticide dissipation models. The empirical formulations of settling rates can be found in  
313 Table A.1. The first formulae (i) estimates the settling rate  $v_s$  according to Stokes equation for  
314 laminar conditions (Reynolds number  $Re < 500$ ). Fiener et al. (2003) computed the settling  
315 rates of particles of different sizes in a vegetated wetland. It was observed that particles  $>63$   
316  $\mu\text{m}$  (i.e., sand) were fully sedimented, whereas particles  $2 \mu\text{m} < x < 63 \mu\text{m}$  (i.e., silt) were  
317 moderately sedimented (up to 26%). In contrast, only 4% of fine particles  $<2 \mu\text{m}$  (i.e., clay)

318 settled on the sediment bed. It was also noticed that settling primarily occurred on the side-  
319 slopes with small Re. The second formulation (ii) suggested by Kadlec et al. (2008) allows  
320 calculating the settling rate in both laminar and turbulent flow based on a drag coefficient  $C_D$   
321 that depends on Re. Formula (ii) assumes that settling results from density difference between  
322 suspended particles and water, so it expresses the rate of a single and isolated spherical  
323 particle. The limit of the first (i) and second method (ii) are the required parameters since in  
324 artificial ponds, neither the density nor the particle size is known. In addition, particles are not  
325 spheres or discs and can agglomerate to a larger size. The formula (iii) estimates the settling  
326 rate of suspended particles in wetlands (Hawley et al., 2014). This formulation required more  
327 parameters such as the water kinematic viscosity since it is adapted for also non-spherical  
328 particles. However, it was often applied to large size particles.

329 Overall, the formula (i) could be sufficient and easy to use for a simple simulation of PP  
330 settling in laminar flows. If the flow is turbulent with a known Re, formula (ii) would be more  
331 suitable for its accuracy. For formula (ii), particle sizes are often approximated according to  
332 their nature (i.e., clay, silt, sand, and OM). Otherwise, the settling rate could be calibrated if  
333 the required data is available. But still, the majority of settling studies are done on nutrients,  
334 and little is known about pesticides (Hantush et al., 2013; Kalin et al., 2017; Walker Jr et al.,  
335 2011). Regarding behavior, settling seems to be a key process of pesticide accumulation in  
336 pond artificial ponds alimented by surface runoff in erosive areas, especially for hydrophobic  
337 pesticides and coarse PP.

### 338 2.1.2 Resuspension

339 Resuspension is the opposite process of settling, through which PP are transported from the  
340 sediment bed to water. Resuspension depends mainly on the water flow and the water depth in  
341 artificial ponds.

342 Resuspension is likely to occur when water turbulence is important (Siobhan Fennessy et al.,  
343 1994), and high water flow can remobilize settled PP back to the water (Collins, 2004;  
344 Jamieson et al., 2005; Vallet, 2011; Wilkes et al., 2009). It was proved that resuspension was  
345 highly affected by the type and density of vegetation in artificial ponds (Liu et al., 2019;  
346 Schulz et al., 2001). Braskerud (2001) presumed that an increase of 30% in a vegetative  
347 cover, initially less than 20%, could reduce resuspension rates from 40% up to 100%. Rose et  
348 al. (2008) showed that the resuspension rate was divided in half by switching to a vegetated  
349 artificial pond. Some studies suggested that deeper FWS wetlands enhanced settling and  
350 burial rather than resuspension (Brueske et al., 1994; Budd et al., 2011). Resuspension is  
351 likely to occur in the main channel where the water velocity is fast (see section 1.3) (Gaullier  
352 et al., 2020) and is mainly driven by wave action generated by the wind (Hawley et al., 2014).  
353 Other agitation factors may be responsible for particle resuspension, such as wildlife  
354 movements within the artificial pond (i.e., bioturbation), although quantitative studies on this  
355 topic remain scarce. Resuspension was significantly less considered in the literature than  
356 settling. However, resuspension occurred with a slow rate of remobilization ( $v_r \sim 10^{-6}$  mm/s)  
357 (Hawley et al., 2014; Sharifi et al., 2013), while Rijn (1984) suggested that the resuspension  
358 rate  $v_r$  reached the quarter of the settling rate  $v_s$ .

359 Globally, significantly lower concentrations of PP measured at the outlet of wetlands than at  
360 the inlet suggests that the contribution of resuspension in pesticides behavior might be  
361 negligible (Budd et al., 2009; Cryder et al., 2021; Supowit et al., 2016), also resuspension is  
362 more dominant in systems with stronger water flows (i.e., rivers) rather than artificial ponds.

363 In addition, high water flow events are usually short and have a long return period, which  
364 decreases the occurrence of resuspension.

### 365 **2.1.3 Advection, dispersion and diffusion**

366 Among the processes behind pesticide transport within the artificial pond are advection,  
367 dispersion including diffusion. Advection carries pesticides in the same direction as the water  
368 flow. Dispersion results from heterogeneities in flow patterns and is a macroscopic process. In  
369 contrast, diffusion is a microscopic movement of pesticide molecules due to a random  
370 molecular motion (i.e., Brownian motion) (Hamdi, 2007). Dispersion and diffusion processes  
371 result from a concentration gradient of pesticides in artificial pond water and carry pesticides  
372 from highly concentrated areas to low concentrations. Advection, dispersion, and diffusion  
373 allow the homogenization of DP concentrations in the artificial pond.

374 Gaullier et al. (2019) showed that water transport is mainly governed by advection at a high  
375 flow rate. While at low flow rates, both water transport and pesticide mitigation are governed  
376 by hydrodynamic dispersion, including molecular diffusion, resulting in a longer contact time  
377 between pesticides and substrate. Without agitation, pesticide transport is only influenced by  
378 diffusion, while agitation enhances advection and dispersion (Gaullier et al., 2018). Thus,  
379 advection/dispersion is more important in the main channel, while diffusion is more likely to  
380 occur in the dead zones (section 1.3). Moreover, diffusion is slower in the sediment layer pore  
381 water because of its tortuosity and the increased length of the water pathway between pores  
382 (Beulke et al., 2004). When the hydraulic regime is laminar, the diffusion is on the molecular  
383 scale, with a thermal diffusion of the order  $1.4 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$  in pure water. In river water  
384 systems, the water is always turbulent. Thus, the effective diffusion is several orders of  
385 magnitude greater. Still, the given thermal diffusion is considered in wetlands, where water  
386 disperses horizontally, and the flow rate is lower than in rivers (Damalas et al., 2011). For  
387 pesticide molecules, the diffusion coefficients usually range from  $10^{-11}$  to  $10^{-10} \text{ m}^2/\text{s}$   
388 (Kipkoech, 2019). Dispersion, including diffusion, also depend on the internal structure of the  
389 artificial pond. For instance, the dispersion was proved to be greater in artificial ponds with a  
390 larger width (Gaullier et al., 2019), while macrophytes enhance diffusion and the hydraulic  
391 performance of the artificial pond (J. F. Holland et al., 2004).

392 In a pesticide transport equation, advection is expressed by the term  $-v \frac{\partial C_w}{\partial x}$  and dispersion is  
393 expressed by  $D_L \frac{\partial^2 C_w}{\partial x^2}$ . Where  $v$  [ $\text{L} \cdot \text{T}^{-1}$ ] is the water velocity;  $C_w$  [ $\text{M} \cdot \text{L}^{-3}$ ] is the pesticide  
394 concentration in water;  $D_L$  [ $\text{L}^2 \cdot \text{T}^{-1}$ ] is the hydrodynamic dispersion coefficient; with  
395  $D_L = D_e + \alpha_L v$ , where  $D_e$  the effective diffusion coefficient, and  $\alpha_L$  [ $\text{L}$ ] the dispersivity.

396

## 397 **2.2 Transfer of pesticides**

398 Once pesticides reach the artificial pond, they are distributed among water, sediments, TSS,  
399 and vegetation are transferred among artificial pond compartments. DP can be exchanged  
400 between the water column and the solid compartments due to “Sorption” and the atmosphere  
401 during “Volatilization”. Also, DP can become PP when sorbed to TSS.

### 402 **2.2.1 Sorption process**

403 Sorption was commonly reported as an important process in the fate of pesticides in artificial  
404 ponds (Cryder et al., 2021; Fernández-Pascual et al., 2020; Hand et al., 2001). In the  
405 following two subsections, we will first present the sorption theory and analyze study cases of  
406 pesticide sorption in artificial ponds. This review will focus on sorption information directly  
407 related to pesticides' fate in artificial ponds; more detailed knowledge of sorption can be

408 found in the literature (Huang et al., 2003; M. McBride, 1994; Pignatello, 1989; Sposito,  
409 2008)

### 410 2.2.1.1 Sorption theory

411 Physically, *sorption* refers to all exchange processes between a dissolved substance and solid  
412 matter in a solution. Among these exchanges, adsorption and desorption remain the most  
413 studied for pesticide fate in the environment. Adsorption is a physical transfer process of  
414 retaining dissolved substances in water on solid surfaces. The dissolved substances are the  
415 “sorbate,” and the solid surface to which they are bound is called “sorbent” or “substrate.”  
416 *Desorption* is when the substrate releases the sorbate and returns to water (Sposito, 2008).  
417 From now on, the term “sorption” will be used to refer to adsorption plus desorption.

418 Most of the sorption studies are conducted in the laboratory and adapted from OECD 106  
419 guidelines for individual molecules, in which sorption experiments are performed using a  
420 batch equilibration technique (OCDE, 2000). The retention and release of the sorbate on a  
421 substrate at various concentrations and a constant temperature are described by a curve called  
422 “adsorption isotherm” and “desorption isotherm,” respectively. The isotherms represent the  
423 relationship  $C_{se}=f(C_{we})$  during adsorption and desorption equilibrium, where  $C_{se}$  ( $\mu\text{g}\cdot\text{g}^{-1}$ ) and  
424  $C_{we}$  ( $\mu\text{g}\cdot\text{L}^{-1}$ ) are the sorbate concentration in the substrate and the sorbate concentration in  
425 the solution at the equilibrium state, respectively.

426 Based on the thermodynamic equilibria theory that assumes complete reversibility of the  
427 chemical reactions, the adsorption and desorption isotherms should be the same (Strawn et al.,  
428 1999). However, sorption mechanisms are driven by different kinetically controlled reactions  
429 or physical phenomena with a large variability of reaction times going from seconds to years,  
430 emphasizing the kinetic character of sorption (Beulke et al., 2004; Caceres-Jensen et al., 2019;  
431 Cara et al., 2021; Kaur et al., 2018; Mamy et al., 2007; Sparks, 2000; Villaverde et al., 2009;  
432 Wu et al., 2017).

433 A difference between adsorption and desorption kinetic rates to reach the equilibrium is  
434 translated by a mismatch between the adsorption and desorption isotherms curves. This  
435 mismatch is called “pseudo-hysteresis” or “kinetic hysteresis” (Strawn et al., 1999), also  
436 referred to as an “apparent irreversibility” (Bladel et al., 1967; M. B. McBride, 1994). It is  
437 important to clarify that the term “irreversibility” does not mean that the sorbate will not  
438 desorb after its adsorption. Still, it will take a long time to reach the equilibrium state  
439 (Limousin et al., 2007). In other terms, hysteresis means that desorption requires a more  
440 significant amount of energy than needed by adsorption (Bowman et al., 1985; Koskinen et  
441 al., 1979; Wu et al., 1988), which could be caused by experimental artifacts or transformation  
442 of the sorbent (Pignatello et al., 1996).

443 The evaluation of sorption requires the determination of its equilibrium and kinetic properties  
444 (Douven et al., 2015). Sorption kinetics are studied with the most applied chemisorption  
445 models: Pseudo-first-order (PFO), pseudo-second-order (PSO), and Elovich models (Azizian,  
446 2004; Ho, 2006; Ho et al., 1998, 1999; Yuh-Shan, 2004), to describe the temporal evolution  
447 of the sorbed amount of the sorbate. At the same time, sorption equilibrium is commonly  
448 modeled by the Freundlich and Langmuir isotherm models (Azizian et al., 2018; Foo et al.,  
449 2010; McKay, 1995). As the equilibrium of kinetic sorption is reached, isotherm models are  
450 applied. The corresponding equations of kinetic and isotherm models can be found in Table  
451 A.2.

### 452 2.2.1.2 Sorption of pesticides in artificial ponds

453 In the case of artificial ponds, the sorbates are dissolved pesticides (DP), and substrates are  
 454 total suspended solids (TSS) with organic and inorganic compounds, sediments, and  
 455 vegetation (Gregoire et al., 2009; Sahin et al., 2020), which represent development support for  
 456 OM and biofilm. The Freundlich and the linear model are commonly used isotherm models to  
 457 describe pesticide sorption on artificial pond substrates (Liu et al., 2019; Takagi et al., 2012;  
 458 Watanabe et al., 2006; Zhang et al., 2018). Pesticide adsorption is widely described by the  
 459 adsorption coefficient normalized to substrate organic carbon content  $K_{foc}$  and  $K_{oc}$  for the  
 460 linear isotherm:

$$461 K_{foc} = \frac{K_{fads}}{OC} \quad (1)$$

$$462 K_{oc} = K_d/OC \quad (2)$$

463 Where OC (%) is the organic carbon content of the pond substrates,  $K_{fads}$  is the Freundlich  
 464 adsorption coefficient, and  $K_d$  is the distribution coefficient (Table A.2).

465 Vallée (2015) and Passeport et al. (2011b) studied the sorption of 12 pesticides with  
 466 contrasting physicochemical properties on pond substrates (i.e., sediments, vegetation, and  
 467 TSS). Sorption coefficients can be found in Table A.3. Based on the  $K_{fads}$  values,  
 468 epoxiconazole was the highly adsorbed pesticide, followed by prochloraz. Epoxiconazole and  
 469 prochloraz have a  $K_{foc}$  range of  $702\text{--}1962 \text{ mg}^{1-n}_f \cdot \text{L}^n_f \cdot \text{kg}^{-1}$  and  $1222\text{--}8654 \text{ mg}^{1-n}_f \cdot \text{L}^n_f \cdot \text{kg}^{-1}$ ,  
 470 respectively (Lewis et al., 2016), which, according to the Soil Survey and Land Research  
 471 Centre (SSLRC) soil persistence classification system, means that they are lowly mobile  
 472 molecules (PSD, 2005). In contrast, the lowest sorption concerned isoproturon, with the  
 473 lowest  $K_{foc}$  values  $55\text{--}60 \text{ mg}^{1-n}_f \cdot \text{L}^n_f \cdot \text{kg}^{-1}$  (Vallée, 2015), followed by MCPA. The low  
 474 adsorption of MCPA could be due to its anionic form, inducing an electrostatic repulsion of  
 475 negatively charged particles (i.e., clay and OM), as supported by Thorstensen et al. (2001).  
 476 Likewise, Poissant et al. (2008) and Wu et al. (2004) reported that pesticides with higher  $K_{oc}$   
 477 values ( $K_{oc} > 500 \text{ L} \cdot \text{kg}^{-1}$ ) are most likely to be sorbed to pond solid particles, agreeing with  
 478 previous findings (Papp, 2009; Saripalli, 1997). The low solubility of epoxiconazole and  
 479 prochloraz also favored their retention on pond substrates. The literature widely reported that  
 480 low solubility enhances pesticide adsorption (Blachnio et al., 2020; Brusseau et al., 2019; Kah  
 481 et al., 2006). Sorption also depends on the hydrophobicity of the pesticide expressed by the  
 482 octanol-water partition coefficient  $K_{ow}$ . Hijosa-Valsero et al. (2016) analyzed fifty-nine  
 483 compounds in water and sediment samples. They found that herbicides in the sediments had  
 484 an average  $S=194 \text{ mg} \cdot \text{L}^{-1}$  and a  $\log K_{ow} = 3.7$ , while herbicides in the water phase were highly  
 485 soluble  $S = 1395 \text{ mg} \cdot \text{L}^{-1}$  with an average  $\log K_{ow} = 2.24$ . These results support that lowly  
 486 soluble, and hydrophobic pesticides ( $\log K_{ow} > 3$ ) are likely to be sorbed on pond sediments,  
 487 which agrees with O'Geen et al. (2010), that observed a 50% reduction in pesticide  
 488 concentration with  $\log K_{ow} > 4.2$ . Likewise, Tang et al. (2017) found that adsorption rates of  
 489 hydrophobic pesticides were significantly higher on the artificial pond vegetation ( $5.52\text{--}8.84$   
 490  $\text{g m}^{-2} \text{ d}^{-1}$ ) than hydrophilic pesticides ( $\log K_{ow} < 3$ ). These results suggest that sorption may  
 491 be the primary driving process of removing hydrophobic pesticides from the artificial pond  
 492 water.

493 On the other hand, vegetation, biofilm, and the OM and clay content of the substrate have a  
 494 significant role in pesticide sorption in artificial ponds. Barchanska et al. (2019) observed that  
 495 the artificial pond remediation of pesticides due to adsorption on vegetation reached 30%. An

496 extensive vegetation cover can enhance adsorption by increasing the HRT [Gauillier et al.](#)  
497 [\(2020\)](#). A higher HRT increases the contact time between pesticides and pond substrates,  
498 favoring adsorption and generally decreasing desorption, as observed by [\(Mamy et al., 2007;](#)  
499 [Olvera-Velona et al., 2008\)](#).

500 [Passeport et al. \(2011b\)](#) and [Vallée \(2015\)](#) observed higher  $K_{fads}$  on vegetation than in  
501 sediments (Table A.3), showing greater retention on OC-rich substrates. [Moore et al. \(2007\)](#)  
502 and [Sahin et al. \(2020\)](#) also proved that diazinon preferentially sorbed on vegetation surfaces  
503 rather than sediments. In like manner, [Rogers et al. \(2009\)](#) showed that the lowly mobile  
504 chlorpyrifos ( $K_{oc} = 5509 \text{ L.kg}^{-1}$  [\(Lewis et al., 2016\)](#)) adsorption was ten times higher on  
505 vegetation than on sediments, and several other papers demonstrated that adsorption is more  
506 dominant in OC-rich substrates, including vegetation ([Guo et al., 2000; Mahabali et al., 2014;](#)  
507 [Moore et al., 2007; Mugni et al., 2011\)](#). Biofilm was also proven to enhance adsorption for  
508 certain pesticides ([Agudelo et al., 2012; Beecraft et al., 2021\)](#).

509 Desorption was also evaluated and was reported to be less dominant in sediments with high  
510 clay and OC content, especially for lowly soluble pesticides ([Gramlich et al., 2018; Olvera-](#)  
511 [Velona et al., 2008; Passeport et al., 2011b; Song et al., 2021; Vallée, 2015\)](#). In comparison,  
512 greater desorption was observed on some highly soluble pesticides ([Olvera-Velona et al.,](#)  
513 [2008\)](#). Hence, hysteresis was generally observed on OC and clay-rich substrates from which  
514 hydrophobic and lowly soluble pesticides are hardly desorbed ([Hand et al., 2001; Li et al.,](#)  
515 [2003; Vagi et al., 2010\)](#).

516 In addition, kinetic sorption rates showed that desorption was slower than adsorption for six  
517 evaluated pesticides, except for picloram. The reviewed kinetic rates of adsorption and  
518 desorption can be found in Table A.4. The picloram exception can be explained because its  
519 sorption was evaluated in lab conditions. Since, in the experimental sample, there was no  
520 consideration of other processes that may compete with desorption (i.e., transformation). The  
521 interaction between desorption and transformation was also observed by [Sørensen et al.](#)  
522 [\(2006\)](#), noticing that slower desorption of MCPA (coincided with higher microbial  
523 transformation. In fact, unlike laboratory-batch sorption observations, sorption and  
524 transformation processes co-occur under field conditions, favoring the occurrence of  
525 hysteresis in the presence of other competitive processes like transformation and diffusion  
526 into sediment layer micropores ([Mamy et al., 2007; Paszko et al., 2016; Takagi et al., 2012;](#)  
527 [Uchimiya et al., 2012\)](#). In contrast, advection/dispersion enhance sorption by facilitating the  
528 access of DP to the pond substrates ([Gauillier et al., 2018\)](#).

529 Overall, we assume that both adsorption and desorption depend on the clay and OC content of  
530 pond substrates and the properties of pesticides. Adsorption is more dominant for  
531 hydrophobic, lowly mobile, and lowly soluble pesticides, and desorption hysteresis is more  
532 accentuated in clayey and OC-rich pond substrates, especially for highly soluble pesticides.

### 533 **2.2.2 Volatilization**

534 Volatilization is a process through which pesticides are transferred outside the pond, from the  
535 water to the atmosphere. This non-degradative removal process strongly depends on the  
536 pesticide molecule's vapor pressure.

537 There are two regimes controlling volatilization: the atmospherically controlled regime and  
538 the regime controlled by water properties. Most pesticides (80-90%) belong to the  
539 atmospherically controlled regime, where the gas exchange between the water and the



540 atmosphere is only sensitive to the parameterization of atmospheric turbulence, and the  
 541 majority of pesticides belong to it; therefore, we will focus on the atmospherically controlled  
 542 regime. In the atmospherically controlled regime, at a very low dimensionless Henry constant  
 543 ( $<10^{-7}$ ) (equivalent to a vapor pressure  $vp <10^{-5}$  Pa), the volatilization rate is so slow that the  
 544 volatilization half-life is tens to hundreds of years. In that case, volatilization becomes  
 545 insignificant compared to other processes (Jacobs et al., 2012). In that respect, Höllrigl-Rosta  
 546 (2017) classified of volatilization according to the vapor pressure of the pesticide molecule  
 547 (Table A.5).

548 In modeling, volatilization is often described by a first-order kinetic equation (Barchanska et  
 549 al., 2019; Comoretto et al., 2008; Gobas et al., 2018; Inao et al., 1999; Singh et al., 1991;  
 550 Watanabe et al., 2006) :

$$551 \quad \frac{dMw}{dt} = -k_v * Mw \quad (3)$$

552 Where Mw is the mass of the DP, and  $k_v$  ( $d^{-1}$ ) is the pesticide rate constant of volatilization to  
 553 the atmosphere. Volatilization can also be represented by its corresponding half-life  $DT_{50v}$  (d):

$$554 \quad DT_{50v} = \frac{\ln(2)}{k_v} \quad (4)$$

555 Since this transfer process depends on other factors, the volatilization rate may be expressed  
 556 empirically as a function of both pesticide properties and climate conditions. Table A.6 are  
 557 simplified form of the rate of volatilization  $k_v$  used in descriptive models of the fate of  
 558 pesticides. In other studies, there are many complicated formulations (Bunyakan et al., 2006;  
 559 Comoretto et al., 2008), in which  $k_v$  depends on diffusion coefficients, air-water side, water-  
 560 air side mass transfer coefficient, and friction. However, they are usually left for  
 561 volatilization-specific studies and do not model the fate of pesticides in artificial ponds.

562 A bibliographic review of calculated volatilization half-lives  $DT_{50v}$  (d) of certain pesticides  
 563 can be found in Table A.7. For most pesticides in artificial ponds, the vapor pressure is lower  
 564 than  $10^{-5}$  Pa, which enables to neglect the contribution of volatilization to the artificial pond  
 565 dissipation function according to the classification in Table A.5. However, it was  
 566 demonstrated that some pesticides were efficiently removed from water by volatilization  
 567 (Wang et al., 2014; Wang et al., 2019). In an aquatic microcosm under semi-field conditions,  
 568 Laabs et al. (2007) showed that volatilization was a primary reason for high pesticide losses  
 569 from the water shortly after application, especially for non-polar pesticides (i.e., endosulfan,  
 570 chlorpyrifos, and trifluralin). Similarly, Comoretto et al. (2008) reported that oxadiazon had a  
 571  $DT_{50v}$  of 23 days in a rice field, making it more vulnerable to volatilization when compared to  
 572 stable MPCA and pretilachlor.  $k_v$  rates were either calculated using the empirical formulas in  
 573 Table A.6 or estimated in laboratory experiments. Empirical formulations of  $k_v$  show that  
 574 volatilization rates are mainly dependent on water depth, a mass water-air transfer coefficient  
 575 that is a function of the wind speed, the Henry constant (or vapor pressure and solubility), and  
 576 the molecular weight of the pesticide. Pesticides with a  $vp$  lower than  $10^{-5}$  require years to be  
 577 volatilized according to volatilization half-lives in Table A.7, making them virtually non-  
 578 volatile. In contrast, other pesticides such as alphamethrin, molinate, endosulfan, and dieldrin  
 579 need a few days to volatilize, while oxadiazon requires more days to volatilize. With careful  
 580 consideration of the  $vp$  of these substances, we assume that these assumptions agree with the  
 581 classification in Table A.5. These observations showed that most pesticides are non-volatile

582 due to their low vapor pressure. However, there are still some for which volatilization takes  
583 part in their dissipation in artificial ponds.

## 584 **2.3 Transformation of pesticides**

585 In addition to the transport and transfer processes described in sections 2.1 & 2.2, pesticides  
586 face other processes that transform their original chemical structure. They are also designated  
587 as “degradative” processes when attempting to degrade pesticides to non-organic products  
588 (Cessna et al., 2015; Imfeld et al., 2021). The importance of transformation processes in the  
589 artificial pond dissipation efficiency was widely proved. Pesticides can be transformed into  
590 less toxic products or, in the ideal case, wholly degraded to simple mineral products under the  
591 action of the chemical, photochemical, and biological processes (Tournebize et al., 2017).  
592 This section describes the main biotic and abiotic transformation processes to which  
593 pesticides are exposed in the different compartments of the artificial pond.

### 594 **2.3.1 Biotransformation**

595 Biotransformation is a process by which organic substances are transformed by  
596 microorganisms (bacteria, archaea, and fungi) into chemical substances called metabolites,  
597 resulting in some cases in their complete mineralization (García-Rodríguez et al., 2014). If the  
598 microbial transformation is complete, it becomes a transformation, and pesticides are  
599 mineralized to CO<sub>2</sub> and CH<sub>4</sub>. Otherwise, co-metabolism occurs, during which microorganisms  
600 degrade OM substrates, the primary source of nutrients of the bacteria, primarily to produce  
601 enzymes that will break down sequentially the pesticide molecule, representing a secondary  
602 source of nutrients of the bacteria (Arcangeli et al., 1997), resulting in a metabolite.

603 Recently, in a artificial pond system context, some metabolites were less toxic than their  
604 parent pesticides (Kang et al., 2020). However, it remains unknown if other metabolites are  
605 less or more toxic than the mother compounds. Nonetheless, biotransformation has been  
606 extensively shown as a significant removal process for micro-organic pollutants (Hijosa-  
607 Valsero et al., 2010; Langergraber, 2008; Llorens et al., 2011; Lyu et al., 2018; Samsó et al.,  
608 2013; Yang et al., 2017; Zhang et al., 2017).

609 Biotransformation occurs in both aerobic and anaerobic conditions. Aerobic  
610 biotransformation occurs in oxic conditions, mainly near the plant roots or the water surface,  
611 where the amount of dissolved oxygen is high enough. Biotransformation is anaerobic in deep  
612 water and sediment depths with generally dissolved oxygen concentrations below 0.5 mg.L<sup>-1</sup>  
613 (U.S.G.S, 2020). The rhizosphere can also be considered as an aerobic zone since oxygen can  
614 be transported from the plant body to the roots (Maltais-Landry et al., 2009), but researchers  
615 showed that the amount of oxygen released by the plant was too little to be considered in  
616 artificial pond fate models (Bezbaruah et al., 2005; Llorens et al., 2011). Artificial ponds are  
617 mostly aerobic in the water column surface, with anaerobic conditions occurring at the bottom  
618 sediment layer and deep water (Vymazal et al., 2015). The sediment layer was proved to be  
619 characterized by a sharp decrease in oxygen (Martínez-Lavanchy et al., 2015; Stottmeister et  
620 al., 2003; Thomas et al., 2011; Zhang et al., 2010). Karpuzcu et al. (2013), Paszko et al.  
621 (2016) and (Mulligan et al., 2016); Paszko et al. (2016) demonstrated that anaerobic  
622 conditions would result in lower biotransformation rates than under aerobic conditions. It  
623 agrees with the recent study of commonly used herbicides in which Droz et al. (2021)  
624 indicated that acetochlor and S-metolachlor transformation prevailed in the water phase and  
625 seemed insignificant in the sediment.

626 Microbial transformation also depends on temperature and radiation (Burrows et al., 2002),  
627 pH, OM content, and microbial population (Vink et al., 1997). Sahin et al. (2020) reported  
628 that humic substances increase biotransformation rates since they can carry microorganisms to  
629 the pesticide. This effect has been widely investigated (Cai et al., 2017; Ortega-Calvo et al.,  
630 1998; Smith et al., 2009; Tejeda-Agredano et al., 2014), mainly for hydrophobic pesticides.  
631 For instance, atrazine was highly biodegraded when sorbed onto clay-humic acid complexes  
632 (Besse-Hoggan et al., 2009). Likewise, Rong et al. (2019) found that the interfacial reactions  
633 on clay surfaces increased the biotransformation rates of methyl parathion. The exposure  
634 history to pesticides of artificial ponds also influences biotransformation. Johnson et al.  
635 (2004) demonstrated that sites with a higher pesticide exposure history had higher  
636 biotransformation rates due to microbial acclimation and microbial community adaptation.

637 The water level is another controlling factor of biotransformation in the sediment  
638 compartment of artificial ponds. Ma et al. (2018) speculated that a decline in the water level  
639 enhances microbial growth and activity and would modify the structure and function of  
640 microbial communities. The study also emphasized that a water volume drop-off would  
641 enhance aerobic conditions, induce plant succession to the artificial pond center, and stimulate  
642 OM accumulation and mineralization.

643 The aging of sediments also intensifies the sequestration of PP after their settling, thus  
644 decreasing their bioavailability and hindering microbial transformation (Ahmad et al., 2004).  
645 Budd et al. (2011) proved that once pyrethroids were settled, they were stable in dry and  
646 aerobic sediments between irrigation seasons. They were moderately persistent under flooded  
647 and anaerobic conditions, with a  $DT_{50}$  between 106-353 days. This agrees with the  
648 observation of Cryder et al. (2021), showing that adsorption and subsequent settling were the  
649 dominant processes governing the fate of pyrethroids in ponds instead of biotransformation.

650 Vegetation has been widely recognized as an important stimulator of biotransformation  
651 (Moore et al., 2007; Rai, 2009; Stang et al., 2016; Sur et al., 2003; Wang et al., 2017). For  
652 instance, chlorpyrifos removal rate reached  $0.1 \text{ mg}\cdot\text{m}^{-1}\cdot\text{day}^{-1}$  due to biotransformation in  
653 vegetated mesocosms (Tang et al., 2019). Submerged stems and leaves of macrophytes are an  
654 essential habitat for biofilms (Brix, 2003; C. Zhang et al., 2021). These biofilms, along with  
655 those on all other immersed solid surfaces in the artificial pond system - including dead  
656 macrophytes - are stimulators of microbial processing in artificial ponds (Brix, 2003; Dash et  
657 al., 2020; Lv et al., 2017). Several kinds of phototrophic bacteria, algae, and biofilms in the  
658 water-sediment interface and on the surface of macrophytes were proved to be important  
659 agents of pesticides transformation in artificial ponds (Katagi et al., 2016). Although,  
660 biotransformation in the biofilm can be limited sometimes due to the slow kinetics of mass  
661 transfer or enzymatic reactions (Chen et al., 2015).

662 In modeling, biotransformation is often described by a first-order kinetic model (Beringer et  
663 al., 2021; Green et al., 1990; Mamy et al., 2007; Pignatello, 1999; Scow et al., 1996; Torabi et  
664 al., 2020). Where  $k_{\text{bio}}$  ( $\text{d}^{-1}$ ) is the biotransformation kinetic constant in the compartment in  
665 question. Biotransformation can be represented either by the kinetic constant  $k_{\text{bio}}$  ( $\text{d}^{-1}$ ) or by  
666 the corresponding half-life  $DT_{50\text{bio}}$  (d) (see Eq.(3) and Eq.(4)).

667 Several studies managed to estimate the biotransformation rate constants in artificial ponds in  
668 laboratory conditions, through incubation manipulations. Incubation experiments aims to  
669 calculate pesticide concentrations in the different compartments of a contaminated sample

670 (water and sediments). Then, the concentrations are fitted to a first-order kinetic decay model  
671 to estimate the rate constants  $k_{\text{bio}}$  and half-lives  $DT_{50\text{bio}}$ . Table A.8 presents a literature review  
672 of estimated biotransformation half-lives  $DT_{50\text{bio}}$ .

673 The values of biotransformation half-lives (Table A.8) show that hydrophobic pesticides  
674 pretilachlor and fenthion were rapidly biodegraded in sediments; we suggest that it may be  
675 related to the fact that they were mainly sorbed on substrates easily accessible to  
676 microorganisms. Pretilachlor was more rapidly degraded in water ( $DT_{50\text{bio,w}} = 9.8$  d). Even  
677 though being hydrophobic and lowly mobile ( $K_{\text{oc}} = 5509$  L.kg<sup>-1</sup>), chlorpyrifos was more  
678 persistent in sediments than in water columns, and was favorable to aerobic conditions  
679 (O'Geen et al., 2010). Comparing the behavior of pretilachlor, fenthion, and chlorpyrifos, that  
680 hydrophobicity, and low mobility may not necessarily favor biotransformation in sediments  
681 rather than water. On the other hand, biotransformation in sediments seemed relatively slower  
682 for more mobile pesticides (i.e., 2, 4-D, clothianidin, acetochlor, metazachlor, and S-  
683 metolachlor), except for the MCPA. We suggest that MCPA was not expected to sorb on TSS  
684 and sediments due to its low  $K_{\text{oc}}$ . Its transformation might be more favorable under aerobic  
685 conditions (on the water surface) (PubChem, 2021), explaining its short half-life in the water  
686 phase. S-metolachlor was moderately persistent in both water and sediments; this may be  
687 explained by its complex chemical structure that forbids access to enzymes and prevents its  
688 transformation under aerobic and anaerobic conditions (Droz et al., 2021). Finally,  $DT_{50\text{bio}}$   
689 values showed that biotransformation was faster in oxic areas, except for acetochlor ( $DT_{50\text{bio,w}}$   
690 = 47 d) and clothianidin ( $DT_{50\text{bio,w}} = 27.2$  d) that were rapidly transformed under anaerobic  
691 conditions. Although, it is not possible to infer any direct link between the OC content and the  
692 biotransformation rate since sites were in the same range of OC.

693 Compared to the values of the Pesticide Properties Database (PPDB) (Lewis et al., 2016),  
694 biotransformation half-lives were faster when estimated in artificial ponds, and for now, we  
695 cannot make any conclusion about this difference since the conditions to estimate  $DT_{50\text{bio}}$  in  
696 PPDB have not been detailed.

697 Overall, biotransformation is commonly expressed by a first-kinetic order model and  
698 enhanced by increased vegetation within the artificial pond providing OM that supports  
699 microbes and increases the HRT. Therefore, we suggest introducing a modulation coefficient  
700 according to vegetation cover and OC content in water and sediments of a specific site will  
701 increase  $k_{\text{bio}}$  representability. At this time, no rule has been set up for pesticides  
702 biotransformation in artificial ponds: neither a direct link with the pesticide properties has  
703 been highlighted because biotransformation does not act alone, but simultaneously with other  
704 processes. In the future, a more profound exam of biotransformation rates of different  
705 pesticides accounting for their interaction with other processes (i.e., adsorption and settling,  
706 adsorption/desorption, and dispersion/diffusion) is needed. There is a lack of information  
707 concerning biotransformation in vegetation/biofilm compartments. Therefore further studies  
708 should be carried out to estimate corresponding transformation rates and account for a  
709 possible lag phase reflecting microbial acclimation, as shown by Passeport et al. (2011a). In  
710 pesticides databases (i.e., PPDB) there is no distinction between the different compartments  
711 (water, sediments, and vegetation) for biotransformation half-lives, making it hard to compare  
712 and confront the rates measured as a part of artificial pond surveys with those in pesticides  
713 databases.

714 Globally, biotransformation remains a highly changing phenomenon that depends on both the  
715 pesticide properties and the site conditions in which microorganisms can act. Defining

716 specific biotransformation half-life for artificial ponds, would be more informative than the  
717 PPDB  $DT_{50\text{bio}}$  values to estimate the contribution of biotransformation to overall dissipation in  
718 artificial ponds.

### 719 **2.3.2 Photodegradation**

720 Photodegradation or photolysis transforms pesticides exposed to sunlight, especially at  
721 wavelengths below 400 nm. The products formed by sunlight-induced transformations are  
722 known as photoproducts (Gerecke et al., 2001). Photodegradation is one of the significant  
723 abiotic degradation processes in artificial ponds (Lin et al., 2005; Papaevangelou et al., 2017;  
724 Stangroom et al., 2000).

725 Photolysis can be direct or indirect. During direct photolysis, pesticides absorb light energy  
726 and become excited; they can be transformed depending on the availability of the activation  
727 energy. In indirect photolysis, the pesticide reacts with other species produced  
728 photochemically (i.e.,  $CO_3^{\bullet-}$ , hydroxyl radical  $OH^{\bullet}$ , singlet oxygen  $O^1_2$ , and triplet-excited  
729 state dissolved OM (DOM)), causing degradation or conversion into other products (Katagi et  
730 al., 2016; Miller et al., 2005; Pohlman et al., 1983; Zeng et al., 2013; Zepp et al., 1987).  $OH^{\bullet}$   
731 can be produced by nitrate photolysis, even at a concentration as low as  $0.02 \text{ mg.L}^{-1}$  (Vione et  
732 al., 2014). DOM generates DOM\*, the precursor of singlet molecular oxygen ( $O^1_2$ ) in surface  
733 waters. DOM\* and  $O^1_2$  can react with pesticides (Drouin et al., 2021). The most reactive  
734 species is  $OH^{\bullet}$  attacking C-H bonds and mainly controls pesticide photodegradation.

735 Because of the non-ability of solar radiation to penetrate deeper into the water, direct  
736 photolysis remains efficient only in the first centimeters of the artificial pond (Frank et al.,  
737 2002). The effectiveness of photodegradation strongly depends on the shading capacity of the  
738 vegetation canopy and turbidity within the water column, which may attenuate the penetration  
739 of solar radiation (MacIntyre et al., 2006; Rose et al., 2008). This transformation process was  
740 also reported to be positively correlated to the artificial pond water pH (Le Person et al.,  
741 2016). In natural waters, DOM and inorganic compounds are essential absorbers of sunlight  
742 and influence the photochemistry of pesticides in artificial pond (Burrows et al., 2002). In  
743 addition, particulate matter such as sediment particles and microorganisms suspended in the  
744 water column may scatter incident light and prevent the light from penetrating the artificial  
745 pond. This phenomenon is called the quenching effect of OM (Larson et al., 1994; Pattanayak  
746 et al., 2018; Ruiz-Medina et al., 2018). Photochemical degradation would be more efficient in  
747 an open water artificial pond with low turbidity (O'Geen et al., 2010; Vymazal et al., 2015). In  
748 DOC-rich ponds ( $DOC > 20 \text{ mg.L}^{-1}$ ), photolysis is unlikely to be operative in pesticide  
749 dissipation since DOC content massively attenuates UV light transmission to DP (Waiser et  
750 al., 2004). Lagunas-Allué et al. (2010) observed less than an 8% decrease of boscalid caused  
751 by direct photolysis, while the main removal processes were adsorption on OM and plant  
752 uptake. This observation can be explained by the high OM content that prevents light  
753 penetration to pesticides and limits direct photolysis.

754 On the other hand, several herbicide were efficiently removed by indirect photolysis, such as  
755 atrazine, diuron, and chlorpyrifos in a study conducted by Zeng et al. (2013). Mathon et al.  
756 (2019) evaluated the photodegradation of 23 pesticides using in-situ photo-reactors. They  
757 found that 15 pesticides were photodegraded in the summer against 12 in winter, which  
758 showed that photolysis was not directly linked to the season. However, when Mathon et al.  
759 (2019) compared each of the 23 pesticides photolysis direct and direct+indirect experimental

760 half-lives, they found that indirect photolysis enhances the degradation compared to direct  
761 photolysis. Additionally, the contribution of direct and indirect photolysis was studied for 60  
762 pesticides. Direct photolysis predominated for dinitroaniline herbicides, although more than  
763 50% of the total photodegradation rate could be attributed to indirect photolysis for the other  
764 pesticides. This observation supports the relevance of indirect photolysis in artificial ponds  
765 when light attenuation is minimal (Katagi et al., 2016; Zeng et al., 2013).

766 As with most transformation processes, photodegradation was commonly computed with a  
767 first-order kinetic model (Green et al., 1990; Lam et al., 2003; Rose et al., 2008; Watanabe et  
768 al., 2006; Zeng et al., 2013), where  $k_{\text{photo}}$  ( $\text{d}^{-1}$ ) is the photodegradation kinetic constant,  
769 assumed to be the sum of direct and indirect photolysis kinetic rates (Mathon et al., 2019), and  
770  $\text{DT}_{50\text{photo}}$  ( $\text{d}^{-1}$ ) is the photodegradation half-life. Photolysis half-lives that fitted a first-order  
771 kinetic model in pesticide fate models are presented in Table A.9.

772 Photodegradation half-lives show that the slowest pesticides to be photodegraded were mobile  
773 and moderately mobile pesticides, according to their  $K_{\text{oc}}$  values. In contrast, while lowly  
774 mobile pesticides were rapidly photodegraded (Table A.9). Since lowly pesticides are likely  
775 to be sorbed (see section 2.2.1), we propose that they might be indirectly photodegraded once  
776 sorbed on sediments, suspended solids, or plants through chemical reactions with free radicals  
777 in the water-substrate interface.

778 Overall, since the penetration of solar radiation to deeper water is limited, direct photolysis is  
779 considered only in the first centimeters of the artificial pond, depending on the DOC content.  
780 In contrast, indirect photolysis involving excited radicals may be more relevant through  
781 photochemical degradation and is well described by a first-order kinetic rate. We suggest that  
782 introducing a modulating factor taking into consideration vegetation cover and OM limit light  
783 penetration will increase the accuracy of photolysis modeling.

### 784 2.3.3 Hydrolysis

785 Another abiotic transformation process is the hydrolysis of DP, which depends on the pH and  
786 temperature of artificial ponds. Hydrolysis was commonly considered a minor dissipation  
787 process when compared to adsorption, microbial and photochemical degradation. However, in  
788 some cases, hydrolysis played a significant role in the dissipation function of artificial ponds,  
789 especially under alkaline conditions (Bondarenko et al., 2004; Liu et al., 2001; Papaevangelou  
790 et al., 2017; Yu et al., 2019).

791 For instance, chlorpyrifos was proved sensitive to hydrolysis (Liu et al., 2001; Wu et al.,  
792 2002). Experimental studies showed that higher pH ( $> 8$ ) increased the hydrolysis rate of  
793 chlorpyrifos (Agudelo et al., 2010; Baskaran et al., 2003; Sardar et al., 2005), corresponding  
794 to a half-life of 50 days (Liu et al., 2019; Mackay et al., 2006). Similarly, carbaryl insecticide  
795 was mainly degraded by photolysis and hydrolysis in a pond (Wolfe et al., 1978). Hydrolysis  
796 mainly contributed to endosulfan dissipation (Walse et al., 2002) and dichlorvos had a  
797 hydrolysis half-life of 3 days (Tomlin, 2009). In contrast, hydrolysis contributed to less than  
798 2% of boscalid degradation (Lagunas-Allué et al., 2010). Similarly, the hydrolysis half-life of  
799 dieldrin exceeded three months (Singh et al., 1991) and reached 115 and 138 days for  
800 diazinon and fenthion, respectively (Ibanez et al., 2006; Mackay et al., 2006; Sakellarides et  
801 al., 2003). S-Metolachlor and butachlor were also proved to be persistent to hydrolysis with a  
802 half-life of 200-1155 days at different pH (Masbou et al., 2018; Zheng et al., 2001).  
803 Sometimes, change in diurnal pH due to photosynthesis by aquatic algae and macrophytes

804 may result in photo-synthetically-driven alkaline hydrolysis of some pesticides (Katagi, 2006,  
805 2013).

806 Likewise, hydrolysis can be estimated with a first-order kinetic model (Rose et al., 2008;  
807 Wang et al., 2019), where  $k_h(d^{-1})$  is the hydrolysis kinetic constant and  $DT_{50h}(d^{-1})$  is the  
808 hydrolysis half-life. It was reported that the main controlling factor of hydrolysis is pH (Deer  
809 et al., 2001; Farran et al., 1988; Sereshti et al., 2021; Stangroom et al., 2000).

810 Overall, most pesticides that threaten water quality were considered insensitive to hydrolysis.  
811 It may be due to their chemical structure, such as the lack of methyl ester linkage for  
812 sulfosulfuron herbicide (Sabadie, 2002; Saha et al., 2002) and phosphodiester linkages for  
813 organophosphate pesticides (Sahin et al., 2020). In addition, artificial pond water might  
814 generally be beyond the range of alkaline or acidic conditions, making hydrolysis a very slow  
815 process (Rose et al., 2008). Therefore, we assume that hydrolysis could be neglected in  
816 modeling pesticide dissipation in artificial ponds.

817

### 818 3. Discussion

819 After reviewing various research works about pesticide dissipation in artificial ponds, it  
 820 appears that some studied different processes, while others only focused on one specific  
 821 process. Similarly, some surveys investigated the behavior of multiple pesticides while others  
 822 only evaluated one or multiple pesticides from the same chemical group (see section 2).  
 823 Papers evaluating multiple processes often studied one process. Therefore for a better  
 824 understanding of artificial pond processing, this review combines the investigation of multiple  
 825 pesticides behavior with contrasting physicochemical properties and evaluates transport,  
 826 transfer, and transformation processes occurring in the artificial pond compartments (water,  
 827 sediments, and vegetation). In the following subsections, we discuss this critical review's  
 828 main assumptions regarding the processes' controlling factors, the estimation of parameters  
 829 required to model processes, and the hierarchization of processes.

#### 830 3.1 Controlling factors of the processes

831 As described in section 2, the surveyed processes depend on several factors:

- 832 • **The environmental conditions:** hydraulic parameters, temperature, sediments and  
 833 TSS composition (OC, clay content), vegetation cover, solar radiation, pH, and redox  
 834 conditions.
- 835 • **The pesticide physicochemical properties:** mobility  $K_{oc}$ , hydrophobicity  $K_{ow}$  and  
 836 vapor pressure  $vp$ .

837 The hydraulic regime is responsible for the residence time. A long HRT gives time for the  
 838 pesticide to settle, sorb, desorb, or be transformed (Liu et al., 2019; Sahin et al., 2020).  
 839 Another hydraulic parameter is the water column depth; a shallow water depth enhances  
 840 photolysis and biotransformation by increasing the oxygen concentration in artificial ponds.

841 Sediments and TSS composition interfere in the sorption process. As presented in section  
 842 2.2.1, OC content adsorption and clay content increase the trapping of pesticides in sediments  
 843 by favoring desorption hysteresis. Thus, OC and clay content increase the removal of  
 844 pesticides from the artificial pond water. There was no direct link between biotransformation  
 845 half-lives  $DT_{50bio}$  in substrates and their OC content (Table A.11).  $DT_{50bio,s}$  values show that  
 846 the extent of the studied pesticides was not resistant to biotransformation in the sediment  
 847 regardless of the OC content.

848 However, biotransformation half-lives in the water  $DT_{50bio,w}$ , and sediments  $DT_{50bio,s}$  varied  
 849 according to pesticide properties. However, no direct link was observed between half-life  
 850 ( $DT_{50bio}$ ) and pesticide hydrophobicity ( $K_{oc}$ ) (Table A.8). This observation supports our  
 851 hypothesis of process synergy, and that dissipation is explained by the interaction between  
 852 processes (i.e., sorption and transformation) and not a single process.

853 For pesticides properties, the most affecting ones are the  $K_{oc}$  and  $K_{ow}$ , since they control the  
 854 distribution, mobility, and availability of pesticides in the different artificial pond  
 855 compartments. We observed that  $K_{oc}$  and  $K_{ow}$  were determining factors for sorption,  
 856 biotransformation, and photodegradation.

857 We have also noticed that biotransformation half-lives were faster in artificial ponds than  
 858 half-lives in pesticide databases (i.e., PPDB). It should also be noticed that biotransformation  
 859 half-lives are faster in artificial ponds sediments than in agricultural soils (Bolan et al., 1996;  
 860 Passeport et al., 2011a), which support the efficiency and usefulness of artificial ponds.



861 Besides biotransformation, the  $K_{oc}$  and  $\log K_{ow}$  also affect the sorption process. Once lowly  
862 mobile and hydrophobic pesticides are sorbed onto a substrate ( $K_{oc} > 1000 \text{ L.kg}^{-1}$  and  $\log K_{ow}$   
863  $> 3$ ), they become harder to release back into the water. In comparison, more mobile pesticides  
864 ( $K_{oc} < 1000 \text{ L.kg}^{-1}$ ) are continuously transported within the artificial pond. However, it is  
865 unknown whether sorbed pesticides will be trapped in the sediment, suspended solid or  
866 vegetation, or desorbed afterward.

867 Numerous studies proved that vegetation is a determining agent in the fate of pesticides as it  
868 intervenes implicitly in the removal function of artificial ponds. It provides habitat to  
869 microorganisms responsible for pesticide transformation, decreases water velocity to increase  
870 settling, increases the OC content and composition diversity to enhance adsorption, and brings  
871 oxygen to sediments to promote aerobic transformation. In rare cases, vegetation was also  
872 responsible for trapping pesticides due to plant uptake. Nevertheless, it remains complex to  
873 estimate and quantify the effect of plant uptake on the fate of pesticides (Jorda et al., 2021).  
874 Another phytoremediation function of vegetation is through entophytic bacteria living in the  
875 interior tissue of plants that can potentially degrade pesticides. However, the fraction of  
876 pesticides collated in plants were often insignificant ( $< 10\%$ ) (Butkovskiy et al., 2021; Singh  
877 et al., 2021).

878 Temperature is a stimulator for transformation that increases the microbial activity behind  
879 biotransformation, solar radiation is responsible for photodegradation and enhances  
880 hydrolysis.

881

882 We suggest that process interactions affect their contribution to pesticide fate. The strong  
883 relationship between a process and pesticide properties may explain the choice of studying a  
884 specific process and pesticide. For instance, sorption is more involved in hydrophobic  
885 pesticide dissipation. At the same time, volatilization contributes more to the behavior of  
886 pesticides with a significant vapor pressure (Table A.7). On the other hand, PPDB half-life  
887 values can be used to model the behavior of some pesticides if they are close to the half-lives  
888 estimated in laboratory conditions or give satisfactory simulation results close to the  
889 observations.

### 890 **3.2 Parameter estimation for modeling**

891 After the analysis of different formulations, we suggest that processes can be quantified and  
892 hierarchized according to:

- 893 • Kinetic rates  $k$  ( $\text{d}^{-1}$ ) for the transport and transfer processes: adsorption-desorption;  
894 settling-resuspension; and volatilization.
- 895 • Half-lives  $DT_{50}$  (d) for the transformation processes: biotransformation, photolysis,  
896 and hydrolysis.

897 The different methods used to evaluate the previously described processes and their  
898 corresponding parameters are summarized in Table 1.

899

900 **Table 1**

901 Commonly established methods in the literature to quantify and parametrize a process for a pesticide dissipation  
 902 modeling approach in artificial ponds.

| <b>Process</b>        | <b>Method</b>  | <b>Parameter</b>   | <b>Units</b>        |
|-----------------------|--|--------------------|---------------------|
| <b>Transport</b>      |  |                    |                     |
| Settling-Resuspension | Empirical formulas                                   | $v_s; v_r$         | $\text{m.day}^{-1}$ |
| <b>Transfer</b>       |  |                    |                     |
| Adsorption-Desorption | Batch experiments<br>+<br>Kinetic model fitting      | $k_{ads}; k_{des}$ | $\text{day}^{-1}$   |
| Volatilization        | Empirical formulas                                   | $k_v$              | $\text{day}^{-1}$   |
| <b>Transformation</b> |  |                    |                     |
| Biotransformation     | Incubation experiments<br>+<br>Kinetic model fitting | $DT_{50bio}$       | $\text{day}^{-1}$   |
| Photolysis            | Lab experiments                                      | $DT_{50photo}$     | $\text{day}^{-1}$   |
| Hydrolysis            | Empirical formulas                                   | $DT_{50h}$         | $\text{day}^{-1}$   |

903

904 Most studies were conducted on a laboratory scale (batch, microcosms, and mesocosms).  
 905 However, laboratory experiments are less advantageous than the rarely conducted in-situ  
 906 manipulations (Fig. 1). More representative; in-situ manipulations imply a better description  
 907 of the processes and the fate of pesticides while considering the interactions and links  
 908 between the different processes (i.e., between sorption and transformation, sorption and  
 909 dispersion/diffusion), which is not easy to bring out in laboratory conditions. In fact, in  
 910 laboratory experiments, only one process is emphasized and examined independently of other  
 911 processes that usually co-occur in field conditions. This often results in the overestimation of  
 912 dissipation in lab-scale studies.

913 Additionally, not all estimated half-lives are compatible with those available in the PPDB,  
 914 especially biotransformation (Table A.8). This incompatibility may be explained by the  
 915 different sites where parameters were estimated, whereas, for the accessible PPDB data, there  
 916 is no site specification. This observation questions the validity of parameters in the free PPDB  
 917 data and their applicability in a process-based model that aims to describe what is happening  
 918 in the field accurately. Using PPDB values in models increases the uncertainty; therefore, we  
 919 suggest defining a DT50 specific to ponds for each process to use in models. The fact that  
 920 DT50 values in the PPDB are higher than those calculated in-situ shows a greater dissipation  
 921 in pond artificial ponds. Because certain photodegradation half-lives in the literature present  
 922 better compatibility with the PPDB values (Table A.8), they could be a good model fit.

923 Table 2 summarizes the studied processes for each pesticide described in this review and the  
 924 equation used to describe it. We noticed a lack of studies quantifying and modeling  
 925 dissipation processes in artificial ponds because studies are often limited to observing the  
 926 process without a modeling approach. A considerable number of pesticides (55) were studied  
 927 to evaluate their behavior according to previously described processes. However, many of

928 these pesticides have only been evaluated once. Hence, more studies are needed on these  
929 pesticides to compare their behavior and draw more robust conclusions.

930 Some pesticides (i.e., boscalid, chlorpyrifos, and pretilachlor) were evaluated according to  
931 multiple processes, but not necessarily with a modeling perspective (Agudelo et al., 2010;  
932 Laabs et al., 2007; Lagunas-Allué et al., 2010; Rogers et al., 2009; Tang et al., 2019;  
933 Karpuzcu et al., 2013; Mackay et al., 2006; Yu et al., 2019). Only, 57 of the 252 reviewed  
934 articles concern modeling.

935 Little is known about the estimation of biotransformation half-life in artificial pond  
936 compartments, except that macrophytes and algae enhance both adsorption and  
937 biotransformation of DP (Katagi et al., 2016). Similarly, anaerobic biotransformation may  
938 occur in the sediment layer yet is still under-researched (Maillard et al., 2014; Vandermaesen  
939 et al., 2016). Globally, it remains challenging to determine a  $DT_{50\text{bio}}$  in each compartment  
940 with lab experiments due to the different behavior a pesticide may have in each of them. It is  
941 also challenging because laboratory experiments can hardly mimic reproducibly process  
942 interactions occurring in the field. For sorption, vegetation remains the least exploited  
943 compartment since there were few surveys to estimate sorption kinetics on vegetation, its  
944 biotransformation rates, or its uptake rates.

945

946 We propose that the previously mentioned controlling factors (temperature, OM, and  
947 vegetation cover) and their interactions are considered for better accuracy by integrating site-  
948 specific modulating factors in the development of pesticide fate models. Modulating factors  
949 also highlight the temporal variation of process efficiency, such as biotransformation  
950 prevailing during the plant growth period (Vandermaesen et al., 2016). So then the question is  
951 whether it is necessary to include this temporal variation in a process-based model to improve  
952 the accuracy or if, by doing so, the complexity increases.

953

### 954 **3.3 Hierarchization of dissipation processes**

955 This review provides a primary idea about the hierarchization of processes according to their  
956 contribution to the removal function of artificial ponds.

957 As adsorption can only trap pesticides in artificial ponds, degradation (i.e., complete  
958 biotransformation, photolysis, and hydrolysis) contributes more to the artificial pond removal  
959 function since it can permanently eliminate toxic substances from the environment. Although  
960 little is known about whether sorbed pesticides will be degraded or released back into the  
961 environment over time, we assume that sorption is still a key process, as it determines the  
962 distribution and availability of pesticides in artificial pond compartments.

963 Among the transformation processes, the most rapid was biotransformation compared to  
964 photodegradation for some pesticides. By comparing the different half-lives, volatilization  
965 was the slowest process, which is in line with the fact that most pesticides are non-volatile due  
966 to their low vapor pressure ( $<10^{-5}$  Pa). Lastly, hydrolysis appears negligible of most  
967 pesticides.

968 Previous reviews, such as Stehle et al. (2011) and Vymazal et al. (2015), did not find a direct  
969 link between pesticide dissipation or accumulation in artificial ponds and pesticide properties  
970 (i.e.,  $K_{oc}$  vs sorption). We suggest that it is because the fate of pesticides in artificial ponds  
971 does not result from a single process but a combination of different transport, transfer, and

972 transformation processes involving multiple artificial pond compartments. This combination  
973 depends on different conditions (i.e., hydrology, climate, physico-chemical factors, and  
974 vegetation cover). We assume that the most dependent processes are sorption and  
975 biotransformation. For some moderately mobile and hydrophilic pesticides, biotransformation  
976 can be the main dissipation process in a artificial pond. After 42 days, up to 86% of diuron  
977 ( $K_{oc} = 600 \text{ L.kg}^{-1}$ ), atrazine ( $K_{oc} = 100 \text{ L.kg}^{-1}$ ) and terbuthylazine ( $K_{oc} = 318 \text{ L.kg}^{-1}$ ) were  
978 degraded (Anderson et al., 2002; Gregoire et al., 2009; Hijosa-Valsero et al., 2016). Also, the  
979 removal of the moderately mobile triazophos ( $K_{oc} = 308 \text{ L.kg}^{-1}$ ) was mostly achieved by  
980 biotransformation rather than adsorption (Cheng et al., 2007; Imfeld et al., 2009; Meng et al.,  
981 2014; Rani et al., 2001). In contrast, for the highly hydrophobic butachlor ( $\log K_{ow} = 4.5$ ),  
982 adsorption was the main process contributing to its dissipation in microcosm experiments.  
983 Many researchers ascertained that strong adsorption to sediments and limited desorption (also  
984 known as “aging”) might decrease the bioavailability of pesticides and thus limit their  
985 biotransformation (Ahmad et al., 2004; Budd et al., 2011; Chaumet et al., 2021; Lee et al.,  
986 2004; Mulligan et al., 2016). All of these results emphasize the dependency between sorption  
987 and biotransformation.

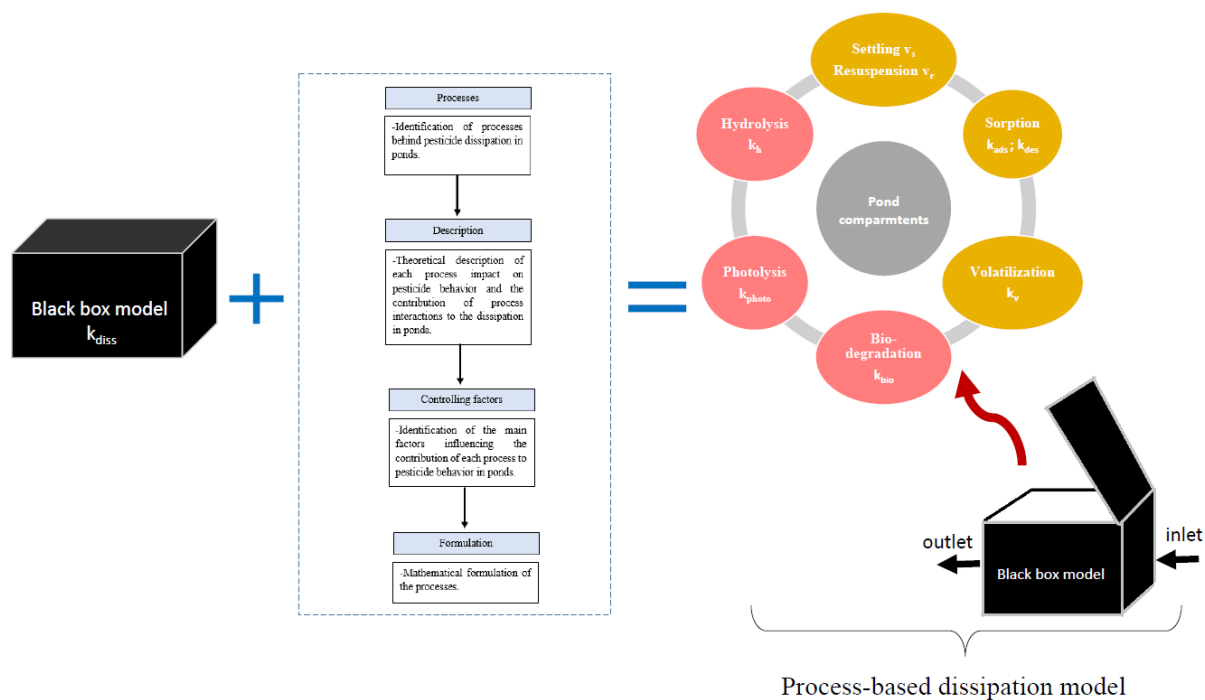
988 When examining citation frequency, some processes (i.e., sorption, biotransformation) were  
989 more cited than others (i.e., settling, resuspension, and volatilization). When a process is not  
990 frequently cited, this could be explained by the difficulty level of its evaluation in both  
991 laboratory and field conditions.

992 The previous conclusions were based on observing removal rates of different processes and  
993 pesticides. The limitations of this approach are the relevance of the statements made based on  
994 a single case study. Nevertheless, describing one survey means that no other case study was  
995 found. The robustness of the conclusions made in this review will be stronger if the same  
996 processes are tested on multiple pesticides and sites with contrasting properties to highlight  
997 the link between the impact of processes and the properties of the pesticides and artificial  
998 ponds.

999  
1000 Identifying the processes with a higher impact can be used to hierarchize processes based on  
1001 their contribution to the dissipation function of artificial ponds. We believe that a  
1002 hierarchization of relevant processes may improve the estimation of the overall efficiency of  
1003 artificial ponds in reducing pesticide transfer into the environment.

1004  
1005 In addition, the black box model does not consider the processes mentioned above and  
1006 describes pesticide behavior with an overall dissipation rate  $k_{diss}$ . Although easy to apply, the  
1007 black box approach does not provide enough information on the behavior of pesticides and  
1008 the contribution of each process to the dissipative function of artificial ponds. Therefore, this  
1009 paper discusses the required elements to develop a simple process-based model involving the  
1010 transfer, transport, and transformation processes in an interplay of artificial pond  
1011 compartments to open the black box (Fig. 3). We assume that a model with multiple process  
1012 rates shows the complexity of modeling the fate of pesticides in artificial ponds; however, it  
1013 can describe and predict pesticide behavior more realistically. We believe this work will  
1014 contribute to a better understanding of artificial pond processing and optimize pesticide fate  
1015 models.

1016



1017  
 1018 **Fig. 3.** Summarized elements and steps detailed in this work in order to develop a process-based model, that  
 1019 contrarily to black models, involves multiple processes in an interplay between different artificial pond  
 1020 compartments.

1021

1022

1023

1024

1025 **Table 2**

1026 List of the surveyed processes for each cited pesticide in the reviewed papers, and the equation used to estimate  
 1027 the rate of processes. NA means that the process was evaluated without a modeling approach.

| Pesticides       | Processes |     |         |          |          |          |          | Source  |
|------------------|-----------|-----|---------|----------|----------|----------|----------|---|
|                  | SET       | RES | SOR     | VOL      | BIO      | PHO      | HYD      |   |
| Acetochlor       |           |     |         |          | Eq. (13) |          |          | (Droz et al., 2021)   |
| Aclonifen        |           |     |         |          | NA       |          |          | (Passeport et al., 2013)  |
| Alphamethrin     |           |     |         | Eq. (11) |          |          |          | (Comoretto et al., 2008)  |
| Atrazine         |           |     | NA      |          | NA       |          |          | (Besse-Hoggan et al., 2009; Moore et al., 2013; Zeng et al., 2013)  |
| Bifenthrin       | NA        |     |         |          |          |          |          | (Cryder et al., 2021)   |
| Boscalid         |           |     | NA      |          | NA       | NA       | Eq. (17) | (Lagunas-Allué et al., 2010; Vallée, 2015)  |
| Butachlor        |           |     | NA      |          | NA       |          | NA       | (Masbou et al., 2018; Torabi et al., 2020; Zheng et al., 2001)  |
| Carbaryl         |           |     |         |          |          |          | NA       | (Wolfe et al., 1978)  |
| Chlorothalonil   |           |     |         |          | NA       |          |          | (Passeport et al., 2013)  |
| Chlorotoluron    |           |     |         |          | NA       |          |          | (Passeport et al., 2013)  |
| Chlorpyrifos     |           |     | NA      | NA       | Eq. (13) |          | NA       | (Agudelo et al., 2010; Laabs et al., 2007; Sardar et al., 2005; Rogers et al., 2009; Tang et al., 2019; Wang et al., 2019; Karpuzcu et al., 2013; Liu et al., 2019; Mackay et al., 2006; Yu et al., 2019) |
| Clothianidin     |           |     |         |          | Eq. (13) |          |          | (Beringer et al., 2021)   |
| Cyfluthrin       | NA        |     |         |          |          |          |          | (Cryder et al., 2021)   |
| Cyproconazole    |           |     |         |          | NA       |          |          | (Passeport et al., 2013)  |
| Diazinon         |           |     | NA      |          | Eq. (13) |          | Eq. (17) | (Ibáñez et al., 2006; Mackay et al., 2006; Sahin et al., 2020; Sakellarides et al., 2003)   |
| Dichlorvos       |           |     |         |          | NA       |          | Eq. (17) | (Sahin et al., 2020; Tomlin, 2009)  |
| Dieldrin         |           |     |         | Eq. (11) |          |          | Eq. (17) | (Singh et al., 1991)  |
| Diuron           |           |     |         |          | NA       |          |          | (Zeng et al., 2013)   |
| Endosulfan       |           |     |         | Eq. (11) |          | Eq. (15) | Eq. (17) | (Rose et al., 2008; Singh et al., 1991; Walse et al., 2002)   |
| Epoxiconazole    |           |     | NA      |          | NA       |          |          | (Passeport et al., 2011; Passeport et al., 2013)  |
| Ethofumesate     |           |     |         |          | NA       |          |          | (Passeport et al., 2013)  |
| Fenitrothion     |           |     |         |          |          | Eq. (15) |          | (Sakellarides et al., 2003)   |
| Fenpropidine     |           |     |         |          | Eq. (13) |          |          | (Passeport et al., 2013)  |
| Fenthion         |           |     |         |          | NA       | Eq. (15) | NA       | (Sahin et al., 2020; Sakellarides et al., 2003)   |
| Fipronil         | NA        |     |         |          |          |          |          | (Cryder et al., 2021)   |
| Fludioxonil      |           |     | NA      |          |          | Eq. (15) |          | (Katagi et al., 2016; Maillard et al., 2014)  |
| Fluometuron      |           |     | NA      |          |          | Eq. (15) | Eq. (17) | (Hand et al., 2001; Rose et al., 2008)  |
| Glyphosate       |           |     | NA      |          |          |          |          | (Maillard et al., 2014)   |
| Imazosulfuron    |           |     |         | Eq. (8)  |          |          |          | (Takagi et al., 2012)   |
| Imidacloprid     |           |     | NA      |          |          |          |          | (Mahabali et al., 2014)   |
| Isoproturon      |           |     | NA      |          | NA       |          |          | (Passeport et al., 2011; Passeport et al., 2013; Vallée, 2015)  |
| Kresoxim-methyl  |           |     |         | Eq. (11) |          |          |          | (Gobas et al., 2018)  |
| Lindane          |           |     | Eq. (8) |          |          |          |          | (Krishna et al., 2008)  |
| MCPA             |           |     | NA      |          | Eq. (13) |          |          | (Comoretto et al., 2008; Sørensen et al., 2006; Thorstensen et al., 2001)   |
| Mefenacet        |           |     | Eq. (8) | Eq. (11) |          |          |          | (Bolan et al., 1996; Watanabe et al., 2006; Yoshida et al., 2000)   |
| Mefenpyr-diethyl |           |     |         | NA       |          |          |          | (Passeport et al., 2013)  |
| Metazachlor      |           |     | NA      |          | Eq. (13) |          |          | (Passeport et al., 2011; Passeport et al., 2013)  |

1028

1029 **Table 2** (continued)

| Pesticides       | Processes |     |         |          |          |          |     | Source   |
|------------------|-----------|-----|---------|----------|----------|----------|-----|--|
|                  | SET       | RES | SOR     | VOL      | BIO      | PHO      | HYD |  |
| Methyl parathion |           | NA  | NA      |          |          |          |     | (Rong et al., 2019; Schulz et al., 2003)   |
| Molinate         |           |     | Eq. (8) | Eq. (11) |          | Eq. (15) |     | (Inao et al., 1999)  |
| Napropamide      |           |     | NA      |          | NA       |          |     | (Passeport et al., 2013; Vallée, 2015)   |
| Oxadiazon        |           |     |         | Eq. (11) |          |          |     | (Comoretto et al., 2008)   |
| Parathion-Methyl |           |     |         |          |          | Eq. (15) |     | (Sakellarides et al., 2003)  |
| Picloram         |           |     | Eq. (8) |          |          |          |     | (McCall et al., 1985)  |
| Pretilachlor     |           |     | Eq. (8) | Eq. (11) | Eq. (13) | Eq. (15) |     | (Vallée, 2015)   |
| Prochloraz       |           |     | NA      |          | NA       |          |     | (Passeport et al., 2013)   |
| Prosulfocarb     |           |     |         |          | NA       |          |     | (Gobas et al., 2018)   |
| Pyraclostrobin   |           |     |         | Eq. (11) |          |          |     | (Maillard et al., 2014)  |
| Pyrimethanil     |           |     | NA      |          |          |          |     | (Droz et al., 2021; Masbou et al., 2018; Passeport et al., 2013)                           |
| S-Metolachlor    |           |     |         |          | Eq. (13) | Eq. (15) | NA  | (Comoretto et al., 2008; Nakano et al., 2004; Watanabe et al., 2006; Yoshida et al., 2000) |
| Spiroxamine      |           |     | NA      |          |          |          |     | (Maillard et al., 2014)  |
| Tebuconazole     |           |     | NA      |          | NA       |          |     | (Maillard et al., 2014; Passeport et al., 2011; Passeport et al., 2013; Vallée, 2015)      |
| Terbutylazine    |           |     |         |          | NA       |          |     | (Hijosa-Valsero et al., 2016)  |
| Triazophos       |           |     |         |          | NA       |          |     | (Cheng et al., 2007)   |
| Trifluralin      |           |     |         | NA       |          |          |     | (Laabs et al., 2007)   |

1030

1031 **4. Conclusion**

1032 The scientific community has widely proved the role and efficiency of artificial ponds in  
 1033 reducing pesticide transfer into the environment. However, few papers have identified the set  
 1034 of processes behind the behavior of pesticides in artificial ponds and opened the black box.  
 1035 The relationship between the dissipation potential of processes and the properties of artificial  
 1036 ponds and pesticides has yet to receive little attention.

1037 When reviewing the literature, we assumed that pesticide behavior is due to multiple  
 1038 processes acting to degrade or trap them in artificial ponds. From this, we can conclude that  
 1039 the fate of pesticides results from the interaction of different processes. These processes  
 1040 depend on several hydraulic, climatic, and physicochemical factors and vegetation cover.  
 1041 Since previous studies have generally focused on a single pesticide or dissipation process, this  
 1042 review combines research work on pesticides with contrasting properties. This extends to  
 1043 pesticide behavior, reflecting several processes involved in the dissipation of pesticides in a  
 1044 large variety of artificial ponds. We also describe and compare the methods used to quantify  
 1045 processes behind pesticide dissipation or accumulation in artificial ponds.

1046 Based on the bibliometric analysis, we explain the citation frequency of a process by the  
 1047 difficulties of evaluating its contribution in the field or the laboratory. Moreover, investigating  
 1048 pesticide behavior in an interplay between transfer, transport, and transformation processes  
 1049 can be used to hierarchize processes based on their contribution to the dissipation function of  
 1050 pond artificial ponds. We suggest that this hierarchization may also improve the estimation of  
 1051 the overall efficiency of pond artificial ponds in pesticide dissipation.

1052 This work is a detailed analysis of the literature to improve our understanding of the potential  
1053 of artificial ponds to dissipate incoming pesticide loads and thus lead to better management  
1054 and, therefore, water quality improvement. This work paves the way for the scientific  
1055 community to develop generic process-based models that, contrary to black-box models, will  
1056 predict pesticide behavior at the artificial pond scale while integrating the key dissipation  
1057 processes.

1058



1059 **Author Contributions:**

1060 Conceptualization: A.B, J.T, S.S, S.P, G.I.; Writing - Original Draft: A.B; Writing - Review  
1061 & Editing: J.T, S.S, S.P, G.I, J.P, B.C; Supervision: J.T, S.S; Project administration: G.I;  
1062 Funding acquisition: G.I, J.T, S.S, S.P, J.P.

1063 **Acknowledgments:**

1064 This work was financially supported by the French National Research Agency ANR [ANR-  
1065 18-CE32-0007], as a part of the project PESTIPOND, and the French National Research  
1066 Institute of Agriculture, Alimentation and Environment.

1067 **Declaration of competing interest:**

1068 The authors declare that they have no known competing financial interests or personal  
1069 relationships that could have appeared to influence the work reported in this paper.

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## Appendix A.

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1074 **Table A.1**

1075 Formulation of settling rates of suspended particles in wetlands and associated parameters.

| Settling rate $v_s$ (m.s <sup>-1</sup> )   | Parameters  | Conditions of application            | Source   |
|--|---|--------------------------------------|--|
| $\frac{2}{9} * \frac{r_p^2 * (\rho_p - \rho_w) * g}{\mu}$ (i)  | <ul style="list-style-type: none"> <li>• <math>v_s</math> (m.s<sup>-1</sup>): Settling rate.</li> <li>• <math>r_p</math> (m): Average radius of the particle.</li> <li>• <math>\rho_p</math> (kg.m<sup>-3</sup>): Particles density.</li> <li>• <math>\rho_w</math> (kg.m<sup>-3</sup>): Water density.</li> <li>• <math>g</math> (m.day<sup>-2</sup>): Gravity.</li> <li>• <math>\mu</math> (kg.m<sup>-1</sup>.day<sup>-1</sup>) : Water viscosity.</li> </ul> | Reynolds number < 500                | (Fiener et al., 2003;<br>Marois et al., 2016;<br>Reddy et al., 2008) |
| $\frac{4}{3} * \frac{g * d}{C_D} * \frac{(\rho_s - \rho_w)^{\frac{1}{2}}}{\rho_w}$ (ii)                      | <ul style="list-style-type: none"> <li>• <math>v_s</math> (m.s<sup>-1</sup>): Settling rate.</li> <li>• <math>d</math> (m): Particles diameter.</li> <li>• <math>\rho_s</math> (kg.m<sup>-3</sup>): Solid density.</li> <li>• <math>\rho_w</math> (kg.m<sup>-3</sup>): Water density.</li> <li>• <math>g</math> (m.j<sup>-2</sup>): Gravity.</li> <li>• <math>C_D = f(\text{Rep})</math>, Rep : Reynolds number of the particle.</li> </ul>                     | Spherical particles in water at 20°C | (Kadlec et al., 2008)  |
| $\mu * d^{-1} * ((25 + 1,2 * d^{*2})^{0,5} - 5)^{1,5}$<br>$d^* = (d * (g * \mu^{-2} * (s - 1))^{1/3})$ (iii) | <ul style="list-style-type: none"> <li>• <math>v_s</math> (m.s<sup>-1</sup>): Settling rate.</li> <li>• <math>d</math> (m): Particles diameter.</li> <li>• <math>g</math> (m.j<sup>-2</sup>): Gravity.</li> <li>• <math>\mu</math> (kg.m<sup>-1</sup>.day<sup>-1</sup>) : Water viscosity.</li> <li>• <math>s</math> : Relative density= <math>f(\rho_s, \rho_w)</math></li> </ul>  | Natural sand particles               | (Hawley et al., 2014)  |

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1077

1078 **Table A.2**

1079 Integrated sorption kinetic and isotherm models. Kinetic models describe the temporal evolution of the sorbed  
 1080 amount of a dissolved substance. Kinetic rates are estimated from fitting laboratory measurements to the kinetic  
 1081 models. Isotherm models describe adsorption and desorption equilibrium. Likewise, isotherm constants are  
 1082 calculated from fitting laboratory measurements to isotherm curves.

| <b>Kinetic models</b>  |   |  |
|--|---|--|
| <b>Equations</b>   | <b>Parameters</b>   | <b>Source</b>                                |
| <p><u>Pseudo first order (PFO):</u></p> $C_s = C_{se} - e^{-k_1 * t}$                            | <ul style="list-style-type: none"> <li>• <math>C_s</math> (<math>\mu\text{g.g}^{-1}</math>): Sorbate concentration in the substrate at instant t.</li> <li>• <math>C_{se}</math> (<math>\mu\text{g.g}^{-1}</math>): Sorbate concentration in the substrate at the equilibrium.</li> <li>• <math>k_1</math> (<math>\text{min}^{-1}</math>): Kinetic constant.</li> </ul>   | <p>(Lin et al., 2009)</p>                    |
| <p><u>Pseudo second order (PSO):</u></p> $C_s = \frac{k_2 * C_{se}^2 * t}{1 + k_2 * C_{se} * t}$ | <ul style="list-style-type: none"> <li>• <math>C_s</math> (<math>\mu\text{g.g}^{-1}</math>): Sorbate concentration in the substrate at instant t.</li> <li>• <math>C_{se}</math> (<math>\mu\text{g.g}^{-1}</math>): Sorbate concentration in the substrate at the equilibrium.</li> <li>• <math>k_2</math> (<math>\text{g.mg}^{-1}.\text{min}^{-1}</math>): Kinetic constant rate.</li> </ul>   | <p>(Boparai et al., 2011)</p>                |
| <p><u>Elovich:</u></p> $C_s = \frac{1}{\beta} * \ln(1 + \alpha * \beta * t)$                     | <ul style="list-style-type: none"> <li>• <math>C_s</math> (<math>\mu\text{g.g}^{-1}</math>): Sorbate concentration in the substrate at instant t.</li> <li>• <math>\alpha</math> (<math>\text{g.mg}^{-1}.\text{min}^{-1}</math>), <math>\beta</math> (<math>\text{g.mg}^{-1}</math>): Kinetic constants.</li> </ul>   | <p>(Chien et al., 1980; Ho et al., 2002)</p> |
| <b>Isotherm models</b>   |   |  |
| <b>Equations</b>   | <b>Parameters</b>   | <b>Source</b>                                |
| <p><u>Freundlich:</u></p> $C_{se} = K_f * C_{we}^{n_f}$  | <ul style="list-style-type: none"> <li>• <math>C_{se}</math> (<math>\mu\text{g.g}^{-1}</math>): Sorbate concentration in the substrate at the equilibrium.</li> <li>• <math>C_{we}</math> (<math>\mu\text{g.g}^{-1}</math>): Sorbate concentration in the water at the equilibrium.</li> <li>• <math>K_f</math> (<math>\text{mg}^{1-n_f}.\text{L}^n.\text{kg}^{-1}</math>): Freundlich constant expressing the molecule-substrate affinity. During adsorption <math>K_f</math> is called <math>K_{fads}</math> and <math>K_{fdes}</math> during desorption.</li> <li>• <math>n_f</math> (unitless): Freundlich constant. When <math>n_f = 1</math>, the kinetic model becomes linear and <math>K_f</math> becomes the classical distribution coefficient <math>K_d</math>.</li> </ul> | <p>(Mckay, 1995)</p>                         |
| <p><u>Langmuir:</u></p> $C_{se} = \frac{K_L * C_{we}}{1 + n_L * C_{we}}$                         | <ul style="list-style-type: none"> <li>• <math>C_{se}</math> (<math>\mu\text{g.g}^{-1}</math>): Sorbate concentration in the substrate at the equilibrium.</li> <li>• <math>C_{we}</math> (<math>\mu\text{g.g}^{-1}</math>): Sorbate concentration in the water at the equilibrium.</li> <li>• <math>K_L</math> (<math>\text{L.g}^{-1}</math>), <math>n_L</math> (unitless): Langmuir constants.</li> </ul>   | <p>(Mckay, 1995)</p>                         |

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1085 **Table A.3**

1086 Non-linear Freundlich isotherm adsorption  $K_{fads}$  ( $\text{mg}^{1-n} \text{kg}^{-1} \text{L}^n$ ) and desorption  $K_{fdes}$  ( $\text{mg}^{1-n} \text{kg}^{-1} \text{L}^n$ ) coefficients.  
 1087 Linear isotherm coefficient  $K_d$  ( $\text{L} \cdot \text{kg}^{-1}$ ) for metazachlor, isoproturon, epoxiconazole, napropamide, boscalid,  
 1088 prochloraz, tebuconazole, glyphosate, pyrimethanil, tetraconazole, fludioxonil and spiroxamine. The sorption  
 1089 coefficients were measured in laboratory conditions with batch experiments on different pond substrates:  
 1090 Sediments, vegetation, and total suspended solids (TSS) (Maillard et al., 2014; Passeport et al., 2011b; Vallée,  
 1091 2015).

| Pesticide     | $K_d/K_f^*$   | Substrates | $K_d$         | $K_{fads}$ | $K_{fdes}$ | Source                   |
|---------------|---------------|------------|---------------|------------|------------|--------------------------|
| Metazachlor   | $K_d = 0.78$  | Sediments  | 3.65          | 4.5        | 0.11       |                          |
|               | $K_f = -$     | Vegetation | 53            | 60         | 3,35       |                          |
| Isoproturon   | $K_d = -$     | Sediments  | 5.85          | 3.5        | 0.1        |                          |
|               | $K_f = 2.83$  | Vegetation | 34            | 44         | 26.5       |                          |
| Epoxiconazole | $K_d = -$     | Sediments  | -             | 281.5      | 0.2        |                          |
|               | $K_f = 12.2$  | Vegetation | 546           | 902        | 2.34       | (Passeport et al., 2011) |
| Napropamide   | $K_d = 21.5$  | Sediments  |               | 5          | 4.8        |                          |
|               | $K_f = 21,6$  | Vegetation |               | 77.4       | 75.2       |                          |
| Boscalid      | $K_d = -$     | Sediments  |               | 9.05       | 8.9        |                          |
|               | $K_f = 12.6$  | Vegetation | -             | 191.8      | 129.5      |                          |
| Prochloraz    | $K_d = -$     | Sediments  |               | 63.3       | 10.3       |                          |
|               | $K_f = 38$    | Vegetation |               | 442.2      | 110        |                          |
| Tebuconazole  | $K_d = -$     | Sediments  |               | 12.3       | 9          |                          |
|               | $K_f = 12.69$ | Vegetation |               | 127.8      | 98.1       | (Vallée, 2015)           |
| Glyphosate    | $K_d = 209.4$ |            | Inlet: 87.06  |            |            |                          |
|               | $K_f = 226.3$ | TSS        | Outlet: 18067 |            |            |                          |
| Pyrimethanil  | $K_d = -$     |            | Inlet: 833.3  |            |            |                          |
|               | $K_f = 8.38$  | TSS        | Outlet: 414   |            |            |                          |
| Tetraconazole | $K_d = -$     |            | Inlet: 524.8  | -          |            |                          |
|               | $K_f = 145$   | TSS        | Outlet: 1533  |            |            |                          |
| Fludioxonil   | $K_d = -$     |            | Inlet: 944.4  |            |            |                          |
|               | $K_f = 3312$  | TSS        | Outlet: 977   |            |            |                          |
| Spiroxamine   | $K_d = -$     |            | Inlet: 1461   |            |            |                          |
|               | $K_f = 142.3$ | TSS        | Outlet: 1681  |            |            | (Maillard et al., 2014)  |

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1093 (\*): Sorption coefficients ( $K_d$ ,  $K_f$ ) were extracted from the pesticide database PPDB (Lewis et al., 2016).

1094 (-): Not measured.

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1097 **Table A.4**

1098 Adsorption and desorption kinetics ( $k_{ads}$ ,  $k_{des}$ ) ( $d^{-1}$ ) of five selected pesticides (imazosulfuron, lindane,  
 1099 mefenacet, molinate and picloram) in different ponds, along with their physicochemical properties  $S$  ( $mg.L^{-1}$ )  
 1100 and  $K_{oc}(L.kg^{-1})$  (Inao et al., 1999; Krishna et al., 2008; Mccall et al., 1985; Takagi et al., 2012; Yoshida et al.,  
 1101 2000). Pesticide properties were extracted from pesticide databases (ChemSpider; Kim et al., 2021; Lewis et al.,  
 1102 2016).

| Pesticide     | Physicochemical properties                | Adsorption $k_{ads}(d^{-1})$ | Desorption $k_{des}(d^{-1})$ | Site  | Source                 |
|---------------|---|------------------------------|------------------------------|---|------------------------|
| Imazosulfuron | $S$ (mg/l) = 1400<br>$K_{oc}(L/kg)$ = 754 | $1.64 \cdot 10^{-1}$         | $7.59 \cdot 10^{-3}$         | Paddy field<br>OC = 1%<br>OM = 1.83%              | (Takagi et al., 2012)  |
| Lindane       | $S$ (mg/l) = 8.5<br>$K_{oc}(L/kg)$ = 1081 | $1.7 \cdot 10^{-4}$          | $8.54 \cdot 10^{-6}$         | Agricultural pond<br>OC=2%<br>Clay=56%            | (Krishna et al., 2008) |
| Mefenacet     | $S$ (mg/l) = 4<br>$K_{oc}(L/kg)$ = 2964   | 1.2                          | $2 \cdot 10^{-1}$            | Paddy field<br>OC = 16%<br>OM = 27%               | (Yoshida et al., 2000) |
| Molinate      | $S$ (mg/l) = 1100<br>$K_{oc}(L/kg)$ = 190 | $4.87 \cdot 10^{-1}$         | $2.9 \cdot 10^{-1}$          | Paddy field<br>OC = 2%,<br>OM=3.44%<br>Clay = 47% | (Inao et al., 1999)    |
| Picloram      | $S$ (mg/l) = 430<br>$K_{oc}(L/kg)$ = 100  | $1.78 \cdot 10^{-1}$         | 3.7                          | Agricultural pond<br>OC= 3%                       | (McCall et al., 1985)  |
| Pretilachlor  | $S$ (mg/l) = 50<br>$K_{oc}(L/kg)$ = 1159  | $1.4 \cdot 10^{-5}$          | $2.3 \cdot 10^{-6}$          | Paddy field<br>OC = 16%<br>OM = 27%               | (Yoshida et al., 2000) |

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1106 **Table A.5**

1107 Volatilization classes according to the vapor pressure values (Höllrigl-Rosta, 2017).

| <b>Vapor pressure (Pa) at 20°C</b>       | <b>Volatilization class</b>   |
|--|---|
| $< 10^{-5}$                              | Non-volatile  |
| $< 10^{-4}$                              | Non-volatile from soil surfaces, no volatilization from greenhouses |
| $10^{-5} < \text{---} < 10^{-4}$         | Semi volatile   |
| $10^{-4} < \text{---} < 5 \cdot 10^{-3}$ | Semi volatile   |
| $\geq 10^{-3}$                           | Volatile  |

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1110

1111 **Table A.6**

1112 Empirical formulations of volatilization rate  $k_v(d^{-1})$  along with their corresponding parameters, based on a 1<sup>st</sup>  
 1113 order kinetic volatilization model.

| Volatilization rate $k_v$  | Parameters  | Source                |
|--|---|-----------------------|
| $\frac{1}{h_w} * \frac{\frac{H}{RT}}{\frac{1}{720 * \sqrt{\frac{18}{MW}}} + \frac{1}{4.8 * \sqrt{\frac{44}{MW}}}}$ | <ul style="list-style-type: none"> <li>• H (Pa.m<sup>3</sup>.mol<sup>-1</sup>): Henry coefficient at 25°C.</li> <li>• R (Pa.m<sup>3</sup>.mol<sup>-1</sup> K<sup>-1</sup>): Universal gas constant.</li> <li>• T (K): Absolute temperature.</li> <li>• MW (g.mol<sup>-1</sup>): Molecular Weight of the chemical compound.</li> <li>• hw (m): Water depth.</li> </ul> | (Jacobs et al., 2012) |
| $\frac{1}{0,0036 + 0,01 * u^{1,2} + \frac{1}{H * (3,6 + 5 * u^{1,2})}}$  | <ul style="list-style-type: none"> <li>• u (m.s<sup>-1</sup>): Wind speed.</li> <li>• H (Pa m<sup>3</sup> g<sup>-1</sup>): Henry constant.</li> <li>• T(°C) : Temperature.</li> </ul>   | (Rose et al., 2008)   |

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1117 **Table A.7**

1118 Review of the volatilization half-lives  $DT_{50v}$  (d) and the corresponding volatilization rates  $k_v$  ( $d^{-1}$ ) in ponds, of  
 1119 different pesticides along with their corresponding vapor pressure  $vp$  (Pa) and their volatilization classification  
 1120 according to the table A.5.

| <b>Pesticide</b> | <b>vp (Pa)*</b>      | <b>Classification</b> | <b><math>DT_{50v}</math> (d)</b> | <b><math>k_v</math> (<math>d^{-1}</math>)</b> | <b>Source</b>            |
|------------------|----------------------|-----------------------|----------------------------------|---|--------------------------|
| Alphamethrin     | $2.3 \cdot 10^{-3}$  | Volatile              | 0.2                              | 3.01  |                          |
| Oxadiazon        | $1.49 \cdot 10^{-5}$ | Semi volatile         | 24.8                             | 0.03  | (Comoretto et al., 2008) |
| Kresoxim-methyl  | $2.29 \cdot 10^{-6}$ | Non-volatile          | 96924                            | 0.00  |                          |
| Pyraclostrobin   | $2.60 \cdot 10^{-8}$ | Non-volatile          | 6850343                          | 0.00  | (Gobas et al., 2018)     |
| Molinate         | 1.3                  | Volatile              | 2.6                              | 0.27  | (Inao et al., 1999)      |
| Endosulfan       | $7.59 \cdot 10^{-1}$ | Volatile              | 3                                | 0.23  |                          |
| Dieldrin         | $3.20 \cdot 10^{-3}$ | Volatile              | 4.4                              | 0.16  | (Singh et al., 1991)     |
| Pretilachlor     | $1.2 \cdot 10^{-4}$  | Semi volatile         | 346.5                            | 0.00  |                          |
| Mefenacet        | $6.39 \cdot 10^{-7}$ | Non-volatile          | 5941                             | 0.00  | (Watanabe et al., 2006)  |

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1122 \*:  $vp$  (Pa) is the vapor pressure of the pesticide at 20°C. The values were extracted from pesticides properties databases  
 1123 PPDB, PubChem and ChemSpider.

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1126 **Table A.8**

1127 Biotransformation half-lives in the water column  $DT_{50bio,w}$  (d) and sediment surface  $DT_{50bio,s}$  (d) of nine  
 1128 pesticides in different wetlands, along with their mobility  $K_{oc}$  ( $L \cdot kg^{-1}$ ) (Beringer et al., 2021; Bondarenko et al.,  
 1129 2004; Comoretto et al., 2008; Droz et al., 2021; Nakano et al., 2004; Passeport et al., 2011a; Passeport et al.,  
 1130 2013; Sahin et al., 2020). These half-lives were confronted to the PPDB values.

| Pesticide     | $K_{oc}^+$<br>(L/kg) | $DT_{50bio,w}$ (d)               | $DT_{50bio,s}$ (d)                       | Site                                | $DT_{50bio,w}$<br>(d)<br>PPDB | $DT_{50bio,s}$<br>(d)<br>PPDB | Source                    |
|---------------|----------------------|----------------------------------|--|-------------------------------------|-------------------------------|-------------------------------|---------------------------|
| Acetochlor    | 156                  | Anaerobic: 59<br>Aerobic: 31     | Anaerobic: 47<br>Aerobic: 53             | Wetland<br>OC=2.3%                  | 40.5                          | 19.7                          | (Droz et al., 2021)       |
| Chlorpyrifos  | 5509                 | -                                | Anaerobic: 125-746<br>Aerobic: 1.8 - 4.9 | Urban stream<br>sediment<br>OC=1.8% | -                             | 36.5                          | (Bondarenko et al., 2004) |
| Clothianidin  | 123                  | -                                | Anaerobic: 27.2<br>Aerobic: 115          | Wetland<br>OC=0.2%                  | -                             | -                             | (Beringer et al., 2020)   |
| Diazinon      | 165-189              | -                                | Aerobic: 53.32                           | Lake sediment<br>OC= 2.22%          | 4.3                           | 10.4                          | (Sahin et al., 2020)      |
| Fenthion      | 1500                 | -                                | Aerobic: 5.5                             |                                     | -                             | 92                            |                           |
| MCPA          | 100                  | -                                | 5.1*                                     | Paddy field<br>OC=0.9%,<br>Clay=47% | -                             | 25                            | (Comoretto et al., 2008)  |
| Metazachlor   | 134                  | 216*                             | 20.6*                                    | Wetland<br>OC = -                   | -                             | -                             | (Passeport et al., 2013)  |
| Pretilachlor  | 1159                 | 9.8*                             | 19.0*                                    | Paddy field<br>OC=2.3%              | -                             | -                             | (Nakano et al., 2004)     |
| S-Metolachlor | 300                  | Anaerobic:<br>199<br>Aerobic: 29 | Anaerobic: 182<br>Aerobic: 151           | Wetland<br>OC=2.3%                  | 88                            | 365                           | (Droz et al., 2021)       |
| Epoxiconazole | 300                  |                                  | 170                                      | Wetland<br>OC=2%                    | 1000                          | 103.6                         | (Passeport et al., 2011)  |

1131

1132 \*: It was not specified under which conditions (aerobic or anaerobic) biotransformation half-lives were measured.

1133 +: The  $K_{oc}$  values were extracted from pesticides databases (ChemSpider; Kim et al., 2021; Lewis et al., 2016; Zambonin et  
 1134 al., 2002).

1135 - : Not available.

1136

1137

1138 **Table A.9**

1139 Photodegradation half-lives in the water column  $DT_{50\text{photo}}$  (d) of eight selected pesticides with different  
 1140 mobilities  $K_{oc}$  ( $L \cdot kg^{-1}$ ). The  $DT_{50}$  values were estimated in (Inao et al., 1999; Katagi et al., 2016; Rose et al.,  
 1141 2008; Sakellarides et al., 2003).

| <b>Pesticide</b> | <b><math>K_{oc}</math> * (L/kg)</b> | <b><math>DT_{50\text{photo}}</math> (d)</b> | <b>PPDB</b> | <b>Source</b>               |
|------------------|-------------------------------------|---|-------------|-----------------------------|
| Atrazine         | 100                                 | 385   | 2.6         | (Mathon et al. 2019)        |
| Dimethoate       | 5.2-50                              | 495   | 175         | (Mathon et al. 2019)        |
| Diuron           | 680                                 | 93.7  | 43          | (Mathon et al. 2019)        |
| Endosulfan       | 11500                               | 12  | -           | (Rose et al., 2008)         |
| Fenitrothion     | 2000                                | 0.5   | 3.5         | (Sakellarides et al., 2003) |
| Fenthion         | 1500                                | 1.6   | 0.4         | (Sakellarides et al., 2003) |
| Fludioxonil      | 145 600                             | 9   | 10          | (Katagi et al., 2016)       |
| Fluometuron      | 202                                 | 1   | stable      | (Rose et al., 2008)         |
| Isoproturon      | 126                                 | 41.3  | 48          | (Mathon et al. 2019)        |
| Molinate         | 190                                 | 54  | stable      | (Inao et al., 1999)         |
| Parathion-Methyl | 1500                                | 25  | 9           | (Sakellarides et al., 2003) |
| Simazine         | 130                                 | 173   | 1.9         | (Mathon et al. 2019)        |

1142 \*: The  $K_{oc}$  values were extracted from pesticides databases (ChemSpider; Kim et al., 2021; Lewis et al., 2016; Zambonin et  
 1143 al., 2002).

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1145

1146 **Table A.10**

1147 Modulating factors applied to the photolysis rate  $k_{\text{photo}}$  to account for controlling factors (i.e., Temperature,  
 1148 depth, and radiation).

| Modulating factors of $k_{\text{photo}}$  | Parameters  | Source                  |
|---|---|-------------------------|
| $\frac{1}{h_w} * \frac{I_0}{I_{\max}} * \frac{1}{25 * TSS * e^{-25 * TSS * z}}$ | <ul style="list-style-type: none"> <li>• <math>z</math> (m): Depth.</li> <li>• <math>I_0</math> (<math>\text{MJ m}^{-2} \text{h}^{-1}</math>): Actual radiation.</li> <li>• <math>I_{\max}</math> (<math>\text{MJ m}^{-2} \text{h}^{-1}</math>): Maximum radiation.</li> <li>• TSS (<math>\text{mg.g}^{-1}</math>): Amount of TSS.</li> </ul> | (Rose et al., 2008)     |
| $R_{UVB-b}$   | <ul style="list-style-type: none"> <li>• <math>R_{UVB-b}</math>: Daily UV-B radiation that penetrates the pond.</li> </ul>  | (Watanabe et al., 2006) |

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1150

1151 **Table A.11**

1152 Biotransformation half-lives  $DT_{50\text{bio},s}$  (d) of five pesticides with different mobilities  $K_{oc}$  and hydrophilicities  $\log$   
 1153  $K_{ow}$ , measured in laboratory studies on sediment substrates with different organic carbon content OC (%) (Vallee  
 1154 et al., 2016). Along with, biotransformation half-lives at the water-sediment interface in wetlands, extracted from  
 1155 the PPDB.

| Pesticides   | $K_{oc}$<br>(L/kg)* | $\log(K_{ow})^*$ | OC (%) | $DT_{50\text{bio},s}$<br>(d) | $DT_{50\text{bio},s}$<br>(d) PPDB |
|--------------|---------------------|------------------|--------|------------------------------|-----------------------------------|
| Boscalid     | 9500                | 2.96             | 1.23   | 39.4                         |                                   |
|              |                     |                  | 1.5    | 29.8                         | 545                               |
|              |                     |                  | 1.7    | 9.4                          |                                   |
| Isoproturon  | 122                 | 2.5              | 1.2    | 100                          |                                   |
|              |                     |                  | 1.5    | 61                           | 149                               |
|              |                     |                  | 1.7    | 63.9                         |                                   |
| Napropamide  | 885                 | 3.3              | 1.23   | 82.7                         |                                   |
|              |                     |                  | 1.5    | 80.1                         | 316                               |
|              |                     |                  | 1.7    | 54                           |                                   |
| Prochloraz   | 378                 | 4.6              | 1.2    | 100                          |                                   |
|              |                     |                  | 1.5    | 17.2                         | 359                               |
|              |                     |                  | 1.7    | 10.2                         |                                   |
| Tebuconazole | 769                 | 3.7              | 1.2    | 30.5                         |                                   |
|              |                     |                  | 1.5    | 30.6                         | 365                               |
|              |                     |                  | 1.7    | 1.4                          |                                   |

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1157 (\*): The physicochemical properties  $K_{oc}$  and  $\log(K_{ow})$  were extracted from the Pesticide Properties DataBase PPDB and  
 1158 PubChem.

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## Appendix B.

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### Methodology

In this paragraph, we will present the methodology adopted to realize this critical review of process formulations and controlling factors behind pesticide dissipation in ponds. This work started with a bibliometric research. We used the listed research equations in different bibliographic research tools\*:

- (constructed wetland) AND ((wastewater OR agricultural) AND treatment)

- pesticide AND (dissipation OR mitigation) AND (wetland OR pond)

- (pesticide OR "Organic pollutant") AND wetland AND model

- (pesticide OR "Organic pollutant") AND wetland AND fate

- pesticide AND *process* AND (pond OR wetland)

- pesticide AND transfer AND (wetland OR pond)

- *process* AND (rate OR model OR kinetic) AND pesticide AND pond

\*: Web of Science (1), Scopus (2), Google Scholar (3), EndNote (4), and Science direct (5).

(1):<https://www.webofscience.com/wos/woscc/basic-search>

(2):<https://www.scopus.com/search/form.uri?display=basic#basic>

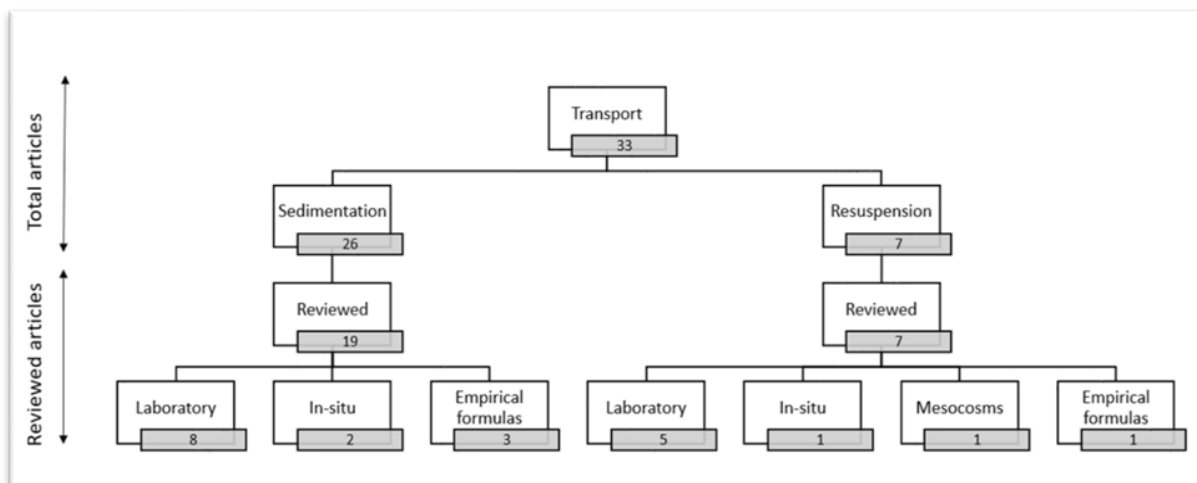
(3): <https://scholar.google.com/schhp?hl=fr>

(4): <https://www.myendnoteweb.com/EndNoteWeb.html>

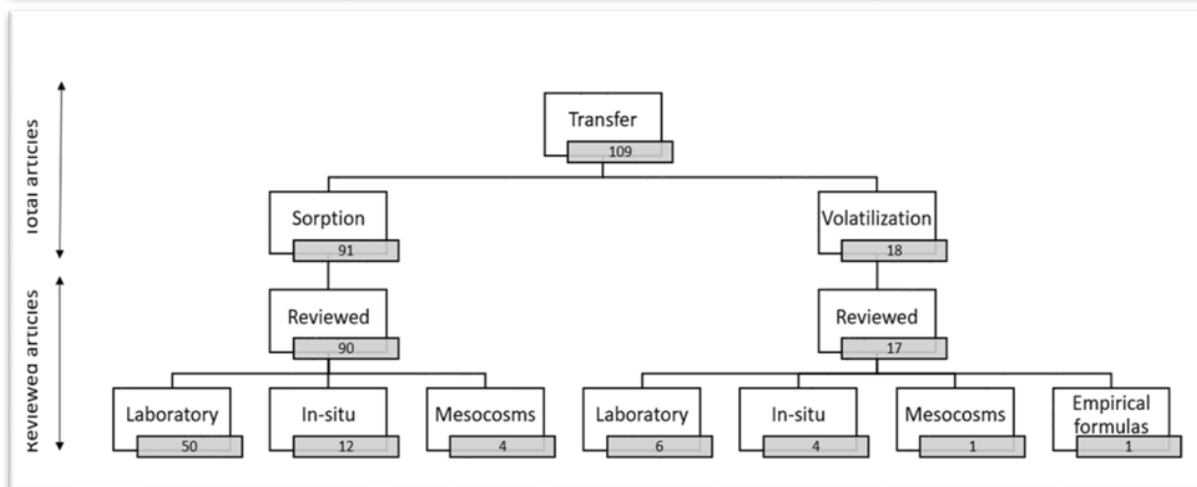
*Italic* represents the name of the processes (i.e., sorption/adsorption/desorption, biodegradation/degradation, settling/sedimentation/burial, resuspension, photolysis/photodegradation, volatilization, and hydrolysis).

First, we looked for general studies about the fate of pesticides in wetlands to record every potential process behind their dissipation. Afterward, we searched for each process whose effect was investigated in ponds on single or multiple pesticides. We selected theoretical papers for the descriptive part of processes and modeling papers to extract the equations for the formulation part in section 3. In each paper, we identified the pesticides targeted, processes investigated, site, and the scale of their evaluation (i.e., laboratory, in-situ) by focusing more on recent work. Given this, three categories of processes in ponds can be distinguished:

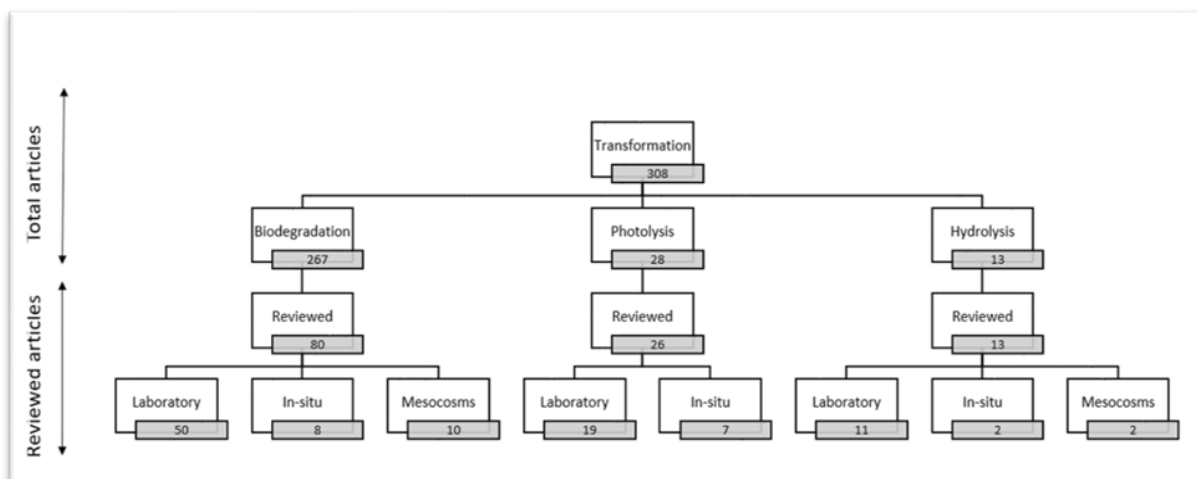
1. Transport is responsible for the fate of pesticides within a compartment of the pond.
2. Transfer controls redistribution of pesticides from a compartment to another.
3. Transformation degrades and modifies the original chemical structure of pesticides.



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1195 **Fig A. 1.** Diagram showing the number of searched articles according to the type of processes, and the number  
 1196 of papers we reviewed. We reviewed papers with the most information about pesticides and processes in ponds.  
 1197 We did not analyze papers with little information, out of context, or redundant. The bottom of the diagram refers  
 1198 to the enumeration of papers according to study scale.

1199 Among the set of processes, according to transformation processes, biodegradation was the  
 1200 most one surveyed with a total of 267 papers, followed by 91 studies of sorption (Fig. 1).  
 1201 Photolysis and settling were less evaluated; only 28 and 26 articles cited them, respectively.  
 1202 Finally, resuspension and volatilization had a minor presence in search results. As for  
 1203 processes formulations, it was necessary to look for modeling papers that either presented a  
 1204 process equation within the framework of a fate model or studied just that specific process.  
 1205 Among the 273 reviewed papers, only 20% were about descriptive models of pesticides in

1206 ponds, and over 80% evaluated more than one pesticide. Although, most of the studies  
1207 investigated a single process for a group of 2-6 pesticides. Most studies aiming to quantify a  
1208 process rate were conducted at a laboratory scale in controlled conditions. They were few  
1209 studies conducted in mesocosms\* and even less in the field.

1210 \*: Mesocosms are experimental water enclosures designed to provide a limited body of water with close to  
1211 natural conditions, in which environmental factors can be realistically manipulated ([Berger et al., 2016](#)).

1212

1213

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